Alfred J. Klapperich
8841 S. Constance Ave.,
Chicago 17, Ill.

АКАДЕМИЯ НАУК СССР
AKADEMIIA NAUK SSSR

OPTICS AND SPECTROSCOPY

JANUARY 1959 · VOL. VI · NO. 1
IANVAR' 1959 · TOM. VI · VYP. 1

Translated on the Initiative of
THE OPTICAL SOCIETY OF AMERICA, INC.
With a Grant-in-Aid from
THE NATIONAL SCIENCE FOUNDATION
by MORRIS D. FRIEDMAN, INC.

RUSSIAN EDITORIAL STAFF

Editor: S. E. FRISH

Assistant Editor: P. P. FEOFILOV

Corresponding Secretary: L. S. SAZONOV

Associate Editors:

M. M. GUREVICH M. A. EL'IASHEVICH A. A. LEBEDEV V. P. LINNIK
S. L. MANDEL'SHTAM I. V. OBREIMOV V. K. PROKOF'EV
N. N. SOBOLEV A. N. TERENIN A. I. TUDOROVSKII

Translation Editorial Staff

DR. JAMES R. ARONSON, *Massachusetts Institute of Technology,*
DR. FRED BEHNKE, *Perkin-Elmer Corp.,*
DR. RICHARD DALVEN, *Raytheon Company, Research Division,*
DR. SUMNER P. DAVIS, *University of California,*
DR. CYRUS FELDMAN, *Oak Ridge National Laboratory*
DR. JOHN S. WAUGH, *Massachusetts Institute of Technology,*
DR. ARTHUR W. WINSTON, *National Research Corp.,*

At its meeting on April 1, 1959, the Board of Directors of the Optical Society of America agreed that:

All members and subscribers will receive both the Journal of the Optical Society of America and an English translation of the Russian journal, "Optika i Spektroskopiia". These two journals will not be available in separate subscriptions but only as a unit.

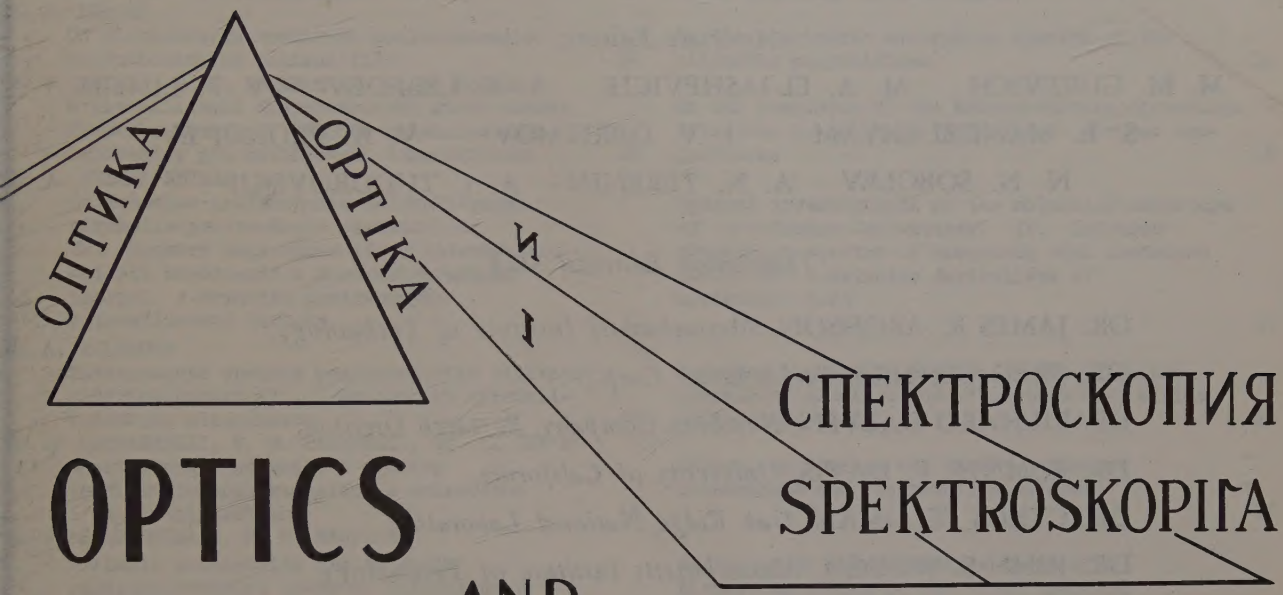
Effective April 1, 1959, the dues for associate members will be $13.00 and for regular members and fellows $17.00. Also effective April 1, the rate for non-member subscriptions will be $25.00 per year. Foreign non-member subscriptions will be at the rate of $25.00 plus $3.00 for postage. A back number single-copy price for "Optics and Spectroscopy" alone is tentatively set at $3.00.

Readers interested in subscribing to these two journals should address their request to the American Institute of Physics, 335 East 45th St., New York, New York. Anyone with an active interest in Optics is eligible for membership in the Optical Society of America. Those wishing to join as an associate member should make a request to Dr. K. S. Gibson, Secretary, Optical Society of America, National Bureau of Standards, Washington 25, D. C. or to any other officer of the Society.

Comments from any reader on articles by the Russian authors in "Optics and Spectroscopy" are invited as "Letters to the Editor" of Journal of the Optical Society of America and should be forwarded to Dr. W. R. Brode, National Bureau of Standards, Washington 25, D. C. These will appear in that section of the Journal of the Optical Society of America.

Application for 2nd Class mailing privileges pending at Post Office, Boston, Mass.

АКАДЕМИЯ НАУК СССР
AKADEMIIA NAUK SSSR



OPTICS AND SPECTROSCOPY

JANUARY 1959 · VOL. VI · NO. 1
IANVAR' 1959 · TOM. VI · VYP. 1

Translated on the Initiative of
THE OPTICAL SOCIETY OF AMERICA, INC.
With a Grant-in-Aid from
THE NATIONAL SCIENCE FOUNDATION
by MORRIS D. FRIEDMAN, INC.

RUSSIAN EDITORIAL STAFF

Editor: S. E. FRISH

Assistant Editor: P. P. FEOFILOV

Corresponding Secretary: L. S. SAZONOV

Associate Editors:

M. M. GUREVICH M. A. EL'IASHEVICH A. A. LEBEDEV V. P. LINNIK
S. L. MANDEL'SHTAM I. V. OBREIMOV V. K. PROKOF'EV
N. N. SOBOLEV A. N. TERENIN A. I. TUDOROVSKII

Translation Editorial Staff

DR. JAMES R. ARONSON, *Massachusetts Institute of Technology,*
DR. FRED BEHNKE, *Perkin-Elmer Corp.,*
DR. RICHARD DALVEN, *Raytheon Company, Research Division,*
DR. SUMNER P. DAVIS, *University of California,*
DR. CYRUS FELDMAN, *Oak Ridge National Laboratory*
DR. JOHN S. WAUGH, *Massachusetts Institute of Technology,*
DR. ARTHUR W. WINSTON, *National Research Corp.,*

At its meeting on April 1, 1959, the Board of Directors of the Optical Society of America agreed that:

All members and subscribers will receive both the Journal of the Optical Society of America and an English translation of the Russian journal, "Optika i Spektroskopiia". These two journals will not be available in separate subscriptions but only as a unit.

Effective April 1, 1959, the dues for associate members will be $13.00 and for regular members and fellows $17.00. Also effective April 1, the rate for non-member subscriptions will be $25.00 per year. Foreign non-member subscriptions will be at the rate of $25.00 plus $3.00 for postage. A back number single-copy price for "Optics and Spectroscopy" alone is tentatively set at $3.00.

Readers interested in subscribing to these two journals should address their request to the American Institute of Physics, 335 East 45th St., New York, New York. Anyone with an active interest in Optics is eligible for membership in the Optical Society of America. Those wishing to join as an associate member should make a request to Dr. K. S. Gibson, Secretary, Optical Society of America, National Bureau of Standards, Washington 25, D. C. or to any other officer of the Society.

Comments from any reader on articles by the Russian authors in "Optics and Spectroscopy" are invited as "Letters to the Editor" of Journal of the Optical Society of America and should be forwarded to Dr. W. R. Brode, National Bureau of Standards, Washington 25, D. C. These will appear in that section of the Journal of the Optical Society of America.

Application for 2nd Class mailing privileges pending at Post Office, Boston, Mass.

TOM VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar', 1959
VOL. VI, No. 1 OPTICS AND SPECTROSCOPY January, 1959

SODERZHANIE

IU. P. DONTSOV
Izotopicheskoe smeschchenie v spektre ZrI 3

G. V. VEINBERG
Izotopicheskii analiz po spektru pogloshcheniia iodistoi medi 9

M. P. VANIUKOV, A. A. MAK, V. R. MURATOV
Vremennye spektry izlucheniia iskrovogo razriada v inertnykh gazakh 17

T. K. REBANE
Ob elektronnykh spektrakh pogloshcheniia alifaticheskikh polisul'fidov 24

M. S. BRODIN, A. F. PRIKHOT'KO, M. S. SOSKIN
O nesobliudenii dispersionnykh sootnoshenii Kramersa-Kroniga v sluchaw molekuliarnykh kristallov pri razlichnykh temperaturakh 28

A. I. FINKEL'SHTEIN
Opticheskoe issledovanie molekuliarnogo stroeniia proizvodnykh s-triazina. IV. Spektry pogloshcheniia v infrakrasnoi oblasti soedinenii s kondensirovannymi iadrami s-triazina-proizvodnykh tsiamellurovoi kisloty 33

V. A. KOLESOVA
Infrakrasnye spektry pogloshcheniia silikatov soderzhashchikh Al , i nekotorykh kristallicheskikh aliuminatov 38

N. A. CHUMAEVSKII, V. M. TATEVSKII, IU. K. IUR'EV
Spektry pogloshcheniia i spektry kombinatsionnogo rasseianiia selenofena i ego metilgomologov 45

A. I. SOKOLOVSKAIA, S. G. RAUTIAN
Vliianie pokazatelia prelomleniia rasseiavaiushchei sredy na intensivnost' linii kombinatsionnogo rasseianiia sveta 51

V. L. LEVSHIN, E. G. BARANOVA
Issledovanie prirody kontsentratsionnogo tusheniia liuminestsentsii krasitelei v raznykh rastvoriteliakh i razdelenie razlichnykh vidov tusheniia 55

S. F. KILIN, I. M. ROZMAN
O zakone vysvechivaniia polistirola pri vozbuzhdenii elektronami 65

S. F. KILIN, I. M. ROZMAN
Vliianie reabsorbtsii na dlitel'nost' fluorestsentsii organicheskikh veshchestv 70

I. N. SHKLIAREVSKII, V. G. PADALKA
Izmerenie opticheskikh postoiannykh medi, zolota i nikelia v infrakrasnoi oblasti spektra 78

F. I. FEDOROV
K teorii opticheskoi aktivnosti kristallov. I. Zakon sokhraneniia energii i tenzory opticheskoi aktivnosti 85

KRATKIE SOOBSHCHENIIA

K. N. TARASOV
Interferentsionnye zerkala na aliuminievoi podlozhke 94

E. M. AKIMOV, I. P. MALKOV
Opredelenie temperatury vakuumnoi iskry 96

A. N. FAIDYSH, V. L. ZIMA
Vliianie kontsentratsii primesi na zavisimost' kvantovykh vykhodov liuminestsentsii ot tolshchiny kristallov antratsena 98

V. M. PIVOVAROV
Vliianie vnutrennogo polia na intensivnost' kombinatsionnogo rasseianiia 101

CONTENTS

Isotopic shift in the spectrum of ZrI 1

Isotopic analysis of the absorption spectrum of copper iodide 4

Time resolved spectra of the radiation from a spark discharge in inert gases 8

On the electronic absorption spectra of the aliphatic polysulfides 11

On the breakdown of the Kramers-Kronig dispersion relations in molecular crystals at various temperatures 14

Optical investigation of the molecular structure of s-triazine derivatives. IV. Infrared absorption spectra of compounds with condensed nuclei of s-triazine derivatives of cyameluric acid 17

Infrared absorption spectra of the silicates containing aluminum and of certain cryatalline aluminates 20

Absorption spectra and Raman spectra of selenophene and its methyl homologues 25

Influence of the refractive index of a dispersing medium on the Raman spectrum line intensity 29

A study of the concentration extinction of dyes in various solutions and isolation of various types of extinction 31

On the fluorescence law in polystyrene on excitation by electrons 37

Effect of reabsorption on the fluorescence lifetimes of organic substances 40

Measurements of the optical constants of copper, gold and nickel in the infrared region of the spectrum 45

On the theory of optical activity in crystals. I. The law of conservation of energy and the optical activity tensors 49

BRIEF REPORTS

Interference mirror on an aluminum substrate 54

Determination of the temperature of a vacuum spark 56

Influence of impurity concentration on the quantum efficiency of luminescence as a function of anthracene crystal thickness 58

Influence of the internal field on Raman spectrum intensity 60

M. G. KAMINSKII
K voprosu o "ballisticheskov" metode issledovaniia zatukhaniia fosforestsentsii 103
On the question of the ballistic method to investigate the decay of phosphorescence 62

I. PASTRNIAK
Spektr infrakrasnogo pogloshcheniia zakisi medi 107
Infrared absorption spectrum of cuprous oxide 64

M. G. GONIKBERG, KH. E. STERIN, S. A. UKHOLIN, A. A. OPEKUNOV, V. T. ALEKSANIAN
Poluchenie spektrov kombinatsionnogo rasseianiia pri vysokikh davleniiakh 109
Production of Raman spectra at high pressures 66

V. A. LOGINOV
Poluchenie spektra pogloshcheniia AlO metodom elektricheskogo vzryva provolochki v vozdukhe pri atmosfernom davlenii 111
Production of the absorption spectrum of AlO by the method of electrically exploding a wire in air at atmospheric pressure 67

IA. I. RYSKIN
Ob infrakrasnykh spektrakh pogloshcheniia nitratov v nevodnykh rastvorakh 113
On the infrared absorption spectra of nitrates in anhydrous solutions 69

E. F. GROSS, L. G. SUSLINA
Monokristally ZnS i spektr ikh kraia pogloshcheniia pri nizkikh temperaturakh 115
Monocrystals of ZnS and the spectrum of their absorption region at low temperatures 70

T. P. BELIKOVA
Dlitel'naia liuminestsentsiia kristallov dibenzila i difenilamina pri foto- i β -vozbuzhdenii 117
Prolonged luminescence of dibenzyl and diphenylamine crystals under photo- and β-excitation 72

A. F. PRIKHOT'KO, M. T. SHPAK
O prokhozhdenii nekotorykh elektronnykh perekhodov v kristallakh naftalina 119
On the origin of certain electronic transitions in naphthalene crystals 73

N. G. PREOBRAZHENSKII
O raspredelenii intensivnosti po konturu spektral'noi linii, sposobnoi k samoobrashcheniiu 120
On intensity distribution along the contour of a self-reversible spectral line 74

KHRONIKA
NEWS

CH. B. LUSHCHIK, A. V. MOSKVIN
VII Sovexhchenie po liuminestsentsii (Kristallofosfory) 122
VII Conference on luminescence (Crystal Phosphors) 76

N. A. TOLSTOI
Optika na mezhdunarodnom kongressa po fizike tverdogo tela (Briussel', 1958 g) 124
Optics at the international congress on the physics of solids (Brussels, 1958) 78

IUBILEI I DATY
ANNIVERSARIES AND DATES

M. A. EL'IASHEVICH (K piatidesiatiletiiu so dniia rozhdeniia) 127
M. A. EL'IASHEVICH (On his fiftieth birthday) 80

Abbreviations of Russian journals and institutes 81
Information for authors (Russian) 82
Letter from the publisher 83

Printed by Blackburn Printing Company, Concord, Mass.

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January, 1959

Isotopic Shift in the Spectrum of ZrI

IU. P. DONTSOV

Abstract: Using a tube with a hollow cathode cooled by liquid nitrogen and a Fabry-Perot interferometer joined with an ISP-51 three-prism spectrograph, an investigation has been made of the isotopic structure of the spectrum of zirconium. The results are tabulated as values of the isotopic shift between pairs of isotopes. The classification of certain lines of the neutral zirconium atom has been clarified. An estimate has been made of the volume effect between the isotopes Zr^{90} and Zr^{92} .

INTRODUCTION

The isotopic shift of spectral lines has been explained as due to two effects: A change in the mass of the nucleus, the mass effect, and a change in the field of the nucleus, the so-called volume effect. Both effects are small in magnitude in elements in the middle of the periodic table, and as a rule, act in opposing directions. Consequently, the isotopic shift in the spectra of these elements has been investigated to a considerably lesser extent than in the spectra of the light and heavy elements. Nevertheless, this study is of great interest since certain information on the change in the radius of the nucleus can be obtained from the magnitude and behavior of the volume part of the shift for the change from isotope to isotope.

A sharp change in the radius of the nucleus is expected upon the addition of a pair of neutrons to a closed shell, which should appear as a "jump" in the isotopic shift. This is corroborated by a measurement of the shift in the region N = 82 [1] and N = 126 [2] . The presence of the same "jump" for N = 50 has not been proved experimentally up to the present. In this connection, a study of the isotopic shift in the spectrum of zirconium is of particular interest since the nucleus of one of the isotopes consists of fifty neutrons.

EXPERIMENTAL DETAILS

The spectrum of zirconium was excited in an aluminum discharge tube with a hollow cathode, cooled by liquid nitrogen, operating at a current of 150 ma . The pressure of the argon, used as the working gas, was 0.5 mm Hg . A Fabry-Perot interferometer, internally mounted in an ISP-51 three-prism spectrograph with a UF-84 camera, was used as the high-resolving power instrument. The interferometer temperature was thermostatically controlled and was maintained constant to $\pm$ 0.05° C accuracy.

The isotopic structure in the spectrum of zirconium appeared to be smaller than the half-width of the spectral lines; consequently, the spectra of enriched samples [3] were photographed separately in succession in order to measure the isotopic shift on a single plate. To do this, a vacuum apparatus was constructed which would permit four discharge tubes to be brought alternately onto the optical axis of the spectrograph by means of rotation around the vertical axis. Using a rotating prism fixed in the upper part of the spectrograph slit, a reference line was superposed along each spectrum. The position of ten interference maxima relative to the reference line were measured on an Abbé comparator for the same zirconium line in all the spectrograms thus obtained. Further computations were made of the isotopic shift by using the method of Tolansky parallelogram tables [4] just as if all the isotopic components were on one spectrogram. The constancy of the interferometer pattern relative to the reference line was verified for the transition from one spectrum to another by the position of the interference rings of one of the argon lines.

The research was conducted on enriched samples. However, because impurities of other isotopes (see Table 1) were also contained in each of the samples in addition to the basic isotope, the shift measured on the plate differs from the actual shift. Consequently, it was necessary to take the superposition of the spectral line contours in order to determine the actual isotopic shift in the spectrum of zirconium. Since the half-width of the spectral lines was larger than the shift between the isotope components, the taking of this factor into account can be done analytically. As a result, the following expressions were obtained, within the accuracy of experimental error, for the magnitudes of the real isotopic shift as a function of the observed shift:

$$\Delta\nu_{90\text{-}92}^{(\text{true})} = 1.12\Delta\nu_{90\text{-}92}^{(\text{obs.})}$$

$$\Delta\nu_{92\text{-}94}^{(\text{true})} = 1.20\Delta\nu_{92\text{-}94}^{(\text{obs.})}$$

$$\Delta\nu_{94\text{-}96}^{(\text{true})} = 2.13\Delta\nu_{90\text{-}96}^{(\text{obs.})} =$$

$$= 1.56\Delta\nu_{92\text{-}94}^{(\text{obs.})} - 1.69\Delta\nu_{90\text{-}92}^{(\text{obs.})} - 0.10\Delta\nu_{90\text{-}91}^{(\text{obs.})}$$

$$\Delta\nu_{90\text{-}91}^{(\text{true})} = 1.26\Delta\nu_{90\text{-}91}^{(\text{obs.})} - 0.09\Delta\nu_{90\text{-}92}^{(\text{obs.})} - 0.02\Delta\nu_{92\text{-}94}^{(\text{obs.})}.$$

Table 1

Sample number	Zr^{90}	Zr^{91}	Zr^{92}	Zr^{94}	Zr^{96}
1	95.8	1.3	1.5	1.2	0.2
2	11.0	79.5	6.1	3.0	0.4
3	6.2	2.0	88.6	3.0	0.2
4	7.8	1.8	3.5	85.5	1.4
5	21.8	5.5	8.4	16.3	48.0

EXPERIMENTAL RESULTS

The results of the measurements taking the isotopic composition of the samples into account are given in Table 2. Presented in the first column of this table are the wavelengths of the lines investigated, their classification [5] is in the second and the values of the isotopic shift between pairs of isotopes in the rest. The data of Table 2 are the average

of the results of measuring three plates, in addition to those lines for which the isotopic shift has been presented just for one pair of isotopes. In these cases, the measurements were made on one plate.

In all lines, with the exception of three, a negative shift has been observed, i.e., the component of the heavier isotope is shifted toward longer wavelengths. Moreover, it should be noted that the magnitude of the isotopic shift for the same electronic transition is approximately equal for both multiplicities. Presented in Table 3 are the average values of the shift for various kinds of transitions.

In order to determine the volume effect in the spectrum of zirconium, it is necessary to eliminate that part of the total isotopic shift which is determined by the mass effect. Hence, it is necessary to know the magnitude and sign of the specific shift, whose calculation for four electrons is a complex problem. However, starting from the results presented in Table 3, a rough estimate of the volume effect can be made. Actually the shift in lines of the $d^2s^2 - d^2sp$ or $d^3s - d^3p$ type is determined by the sum of mass and volume effects while it is practically just a mass effect in lines of the $d^3s - d^2sp$ type. In the latter case, the specific effect can easily be determined from the values of the total shift. It is seen from Table 3 that the isotopic shift in the lines of the first kind differs from the average values within $\pm 2 \cdot 10^{-3}$ cm^{-1} limits. If the mutual screening of the valence electrons is neglected, the volume effect in these lines must be identical, according to theory. Hence, it follows that a change in the mass effect as a function of the kind of transition does not exceed the limit mentioned. In that case, the difference in the magnitudes of the shift in lines of the first and second kinds of transitions yields an estimate of the volume effect

$$\Delta\nu(90 - 92) = -5 \cdot 10^{-3} \text{ cm}^{-1}$$
$$\Delta\nu(92 - 94) = -2 \cdot 10^{-3} \text{ cm}^{-1}$$
$$\Delta\nu(94 - 96) = -3 \cdot 10^{-3} \text{ cm}^{-1}$$

Hence, although the volume effect in the spectrum of zirconium is at least several times smaller than the mass effect, it nevertheless introduces a noticeable contribution to the total isotopic shift.

The results of Table 3 also permitted the classification of certain spectral lines of the neutral zirconium atom to be clarified.

As is seen from Table 2, two possible transitions correspond to the lines 5680.93, 5620.16, 5448.55 and 4866.06 Å. The magnitude and sign of the isotopic shift in the first three lines permits them to be classified as follows:

5680.93 Å($4d^2 5s^2\ ^3P_1 - 4d^2 5s 5p\ ^3S^0_1$)

5620.16 Å($4d^2 5s^2\ ^3P_2 - 4d^2 5s 5p\ ^3S^0_1$)

and

5448.55 Å($4d^3 5s\ ^5F_4 - 4d^2 5s 5p\ ^5D^0_3$)

Starting from the sign of the shift for the 4866.06 Å line, the more probable of the two transitions is ($4d^3 5s\ ^5F_5 - 4d^3 5p\ ^3G^0_5$), however, the magnitude of the shift favors a transition of the

Table 2

λ	Transition	Δν (91—90)	Δν (92—90)	Δν (94—92)	Δν (96—94)
6143.23	$4d^2 5s^2\ ^3F_3 - 4d^2 5s 5p\ ^3F^0_3$		− 8.5 ± 0.9	− 6.2 ± 0.9	
6134.55	$4d^2 5s^2\ ^3F_2 - 4d^2 5s 5p\ ^3F^0_3$		− 8.7 ± 0.5	− 6.7 ± 0.5	
6127.49	$4d^2 5s^2\ ^3F_4 - 4d^2 5s 5p\ ^3F^0_4$		− 8.8 ± 0.6	− 7.7 ± 0.9	
5935.23	$4d^2 5s^2\ ^3F_2 - 4d^2 5s 5p\ ^3F^0_3$		−11.1 ± 0.7	− 6.5 ± 0.6	
5925.13	$4d^2 5s^2\ ^1D_2 - 4d^2 5s 5p\ ^3S^0_1$		−13.0 ± 1.0	−10.2 ± 1.0	
5797.76	$4d^2 5s^2\ ^3F_3 - 4d^2 5s 5p\ ^3D^0_2$	-3.7 ± 2.0	− 7.3 ± 0.9	− 7.1 ± 0.9	-6.3 ± 2.0
5735.70	$4d^2 5s^2\ ^3F_2 - 4d^2 5s 5p\ ^3D^0_2$		− 9.5 ± 0.7	− 6.8 ± 0.7	
5680.93	$\left\{\begin{matrix} 4d^2 5s\ ^1H_5 - 4d^2 5s 5p\ ^1G^0_4 \\ 4d^2 5s^2\ ^3P_1 - 4d^2 5s 5p\ ^3S^0_1 \end{matrix}\right\}$		−11.5 ± 1.1	− 9.9 ± 0.7	
5664.55	$4d^2 5s^2\ ^1D_2 - 4d^2 5s 5p\ ^1D^0_2$	-5.9 ± 2.0	−12.4 ± 0.5	−10.3 ± 0.5	-7.8 ± 2.0
5620.16	$\left\{\begin{matrix} 4d^2 5s 5p\ ^5F^0_3 - 4d^2 5s 6s\ ^5F_2 \\ 4g^2 5s^2\ ^3P_2 - 4d^2 5s 5p\ ^3S^0_1 \end{matrix}\right\}$		−10.9 ± 1.0	− 9.6 ± 1.2	
5545.42	$4d^2 5s 5p\ ^5F^0_4 - 4d^2 5s 6s\ ^5F_4$		+ 8.3 ± 1.9		
5517.12	$4d^3 5s\ ^5F_4 - 4d^2 5s 5p\ ^3D^0_3$		− 5.9 ± 0.9		
5502.12	$4d^2 5s^2\ ^1G_4 - 4d^2 5s 5p\ ^1F^0_3$		− 9.3 ± 0.7	− 7.2 ± 1.2	
5486.09	$4d^3 5s\ ^5F_2 - 4d^2 5s 5p\ ^5D^0_1$		− 6.7 ± 1.0		
5480.83	$4d^3 5s\ ^5F_3 - 4d^2 5s 5p\ ^5D^0_2$		− 6.3 ± 1.8	− 5.8 ± 1.5	
5448.55	$\left\{\begin{matrix} 4d^3 5s\ ^4F_4 - 4d^2 5s 5d\ ^5D^0_3 \\ 4d^3 5s\ ^5F_3 - 4d^3 5p\ ^3F^0_2 \end{matrix}\right\}$		− 5.6 ± 1.5	− 5.8 ± 1.2	
5440.4	$4d^3 5s\ ^5F_1 - 4d^2 5s 5d\ ^5D_1$		− 5.4 ± 2.0		
5407.62	$4d^3 5s\ ^5F_5 - 4d^2 5s 5p\ ^5D^0_4$	-3.7 ± 2.0	− 5.8 ± 1.2	− 6.3 ± 0.9	-6.1 ± 2.0
5405.13	$4d^2 5s^2\ ^1D_2 - 4d^3 5p\ ^3F^0_2$		−12.7 ± 2.4		
5385.14	$4d^2 5s^2\ ^3P_2 - 4d^2 5s 5p\ ^1D^0_2$	-4.9 ± 2.0	−11.5 ± 1.0	−10.4 ± 1.5	-7.4 ± 2.0
5362.56	$4d^2 5s^2\ ^3P_1 - 4d^2 5s 5p\ ^3D^0_1$		−10.7 ± 1.1	−10.2 — 1.0	
5311.40	$4d^2 5s^2\ ^3P_0 - 4d^2 5s 5p\ ^3D^0_1$		−11.8 ± 1.0	−10.5 ± 1.0	
5277.41	$4d^2 5s^2\ ^3P_1 - 4d^2 5s 5p\ ^3D^0_2$		−11.5 ± 1.2	−10.3 ± 0.9	
5155.45	$4d^3 5s\ ^3G_4 - 4d^3 5p\ ^3G^0_5$		− 5.8 ± 1.0	− 6.6 ± 1.2	
5158.02	$4d^2 5s 5p\ ^5G^0_4 - 4d^2 5s 6s\ ^5F_5$		+ 4.8 ± 1.8		
5133.40	$4d^2 5s^2\ ^3P_2 - 4d^2 5s 5p\ ^3D^0_3$		−10.9 ± 1.2	− 8.2 ± 0.7	
5115.24	$4d^2 5s 5p\ ^5G^0_5 - 4d^2 5s 6s\ ^5F_4$		+ 5.8 ± 1.7		
4883.60	$4d^3 5s\ ^5F_4 - 4d^3 5p\ ^3G^0_4$		−13.1 ± 1.0	− 6.4 ± 0.7	
4866.06	$\left\{\begin{matrix} 4d^3 5s\ ^5F_5 - 4d^3 5p\ ^3G^0_5 \\ 4d^2 5s 5p\ ^5F^0_4 - 4d^2 5s 6s\ ^3F_4 \end{matrix}\right\}$		− 6.8 ± 1.5	− 7.0 ± 1.0	
4851.36	$4d^3 5s\ ^5F_2 - 4d^3 5p\ ^5G^0_2$		−10.7 ± 1.2	−11.2 ± 1.2	
4828.04	$4d^3 5s\ ^5F_2 - 4d^3 5p\ ^3G^0_3$	-4.1 ± 2.0	− 9.4 ± 1.8	− 7.9 ± 1.8	-8.4 ± 2.0
4824.28	$4d^3 5s\ ^5F_3 - 4d^3 5p\ ^5G^0_3$	-3.5 ± 2.0	−12.4 ± 1.2	− 8.8 ± 0.7	-9.0 ± 2.0
4784.92	$4d^3 5s\ ^5F_4 - 4d^3 5p\ ^3G^0_5$	-4.8 ± 2.0	−10.2 ± 1.0	− 6.7 ± 0.9	-9.3 ± 2.0
4772.31	$4d^3 5s\ ^5F_2 - 4d^3 5p\ ^5G^0_3$	-4.7 ± 2.0	−11.5 ± 0.9	− 8.0 ± 0.7	-9.5 ± 2.0
4762.78	$4d^3 5s\ ^3H_4 - 4d^3 5p\ ^3I^0_5$		−15.3 ± 1.8	− 6.4 ± 1.2	
4739.48	$4d^3 5s\ ^5F_5 - 4d^3 5p\ ^5G^0_4$	-6.8 ± 2.0	−12.0 ± 1.0	− 8.6 ± 0.7	-8.7 ± 2.0
4732.33	$4d^2 5s^2\ ^1D_2 - 4d^2 5p\ ^1F^0_3$		−10.5 ± 1.0	− 2.3 ± 1.0	
4710.07	$4d^3 5s\ ^5F_4 - 4d^3 5p\ ^5G^0_5$		−12.9 ± 0.7	− 9.7 ± 0.7	
4688.45	$4d^2 5s^2\ ^3F_4 - 4d^2 5s 5p\ ^3G^0_5$		−11.6 ± 1.0	− 9.4 ± 0.9	
4687.80	$4d^3 5s\ ^5F_5 - 4d^3 5p\ ^5G^0_5$		−12.9 ± 0.6	−10.0 ± 0.6	
4633.98	$4d^2 5s^2\ ^3F_3 - 4d^2 5s 5p\ ^3G^0_4$		−10.5 ± 1.8	− 8.0 ± 2.0	
4575.51	$4d^2 5s^2\ ^3F_2 - 4d^2 5s 5p\ ^3G^0_3$		−10.2 ± 2.2	− 6.0 ± 1.5	
4542.22	$4d^2 5s^2\ ^1D_2 - 4d^2 5s 5p\ ^3D^0_3$		−12.2 ± 1.9	− 6.1 ± 1.8	
4535.74	$4d^2 5s^2\ ^3P_2 - 4d^3 5p\ ^1F^0_3$		−10.2 ± 2.2	− 6.8 ± 2.5	
4507.11	$4d^2 5s^2\ ^3P_1 - 4d^2 5s 5d\ ^3D^0_2$		−13.4 ± 1.8	− 6.2 ± 1.8	
4466.91	$4d^2 5s^2\ ^1D_2 - 4d^3 5d\ ^3D^0_2$		−13.2 ± 2.2	− 4.8 ± 1.8	

($4d^3 5s - 4d^2 5s5p$) type, although a perturbation of the $4d^3 5p\,{}^3G^0_5$ term is also possible here by any of the close-lying terms with the configuration $4d^2 5s5p$. Similarly, it follows from the magnitudes of the shifts in the 5797.76 and 5155.45 Å lines that, in contrast to the transitions presented in Table 2, they probably correspond to a transition of the ($4d^3 5s - 4d^2 5s5p$) type.

Table 3

Type of transition	Number of lines of this type	Δν (90–92)	Δν (92–94)	Δν (94–96)
$d^2s^2\,{}^3F—d^2sp\,{}^3F^0$	4	— 9.3	—6.8	—
$d^2s^2\,{}^3p—d^2sp\,{}^3D^0$	5	—11.6	—9.1	—
$d^2s^2\,{}^3F—d^2sp\,{}^3G^0$	3	—10.8	—7.8	—
$d^3s\,{}^5F—d^3p\,{}^3G^0$	3	—10.9	—7.0	—8.8
$d^3s\,{}^5F—d^3p\,{}^5G^0$	6	—12.1	—9.4	—9.1
Average		—10.9	—8.0	—8.9
$d^3s—p^3sp$	6	— 6.1	—6.3	—6.2
$d^25s5p—d^25s6s$	3	+ 6.3	—	—

DISCUSSION OF THE RESULTS

In order to detect the "jump" around $N = 50$, it is necessary to investigate the isotopic shift between isotopes with a number of neutrons both less than and more than the magic number. Zirconium has no isotopes with a number of neutrons less than 50. It has been shown in recently published research of Hughes [6] that the volume shift between the isotopes of strontium with a number of neutrons less than 50 is zero within the limits of experimental error. Therefore, the estimate of the magnitude of the volume effect between the Zr (90-92) isotopes, made in our work, is an indirect verification of the same "jump" in the isotopic shift for $N = 50$ as in the case of higher magic numbers. The value of the volume effect between the Sr (88-90) isotopes is needed for direct proof.

In addition to the similarity established in the behavior of the isotopic shift around N equal to 50, 82 and 126, a difference is also observed in the spectrum of zirconium. It is this, that $\Delta\nu_{obs.}(90\text{-}92)$ is larger than $\Delta\nu_{obs.}(92\text{-}94)$ and $\Delta\nu_{obs.}(94\text{-}96)$ while the shift between the corresponding pairs of isotopes is identical in the spectra of neodymium and samarium.

All the anomalies in the isotopic shift are explained in the theory of the volume effect developed by Wilets [7], Hill, and Ford by change in the deformation of the nucleus. However, it is known that nuclei containing a magic number of neutrons are spherically symmetric. A deficiency or excess of several neutrons in comparison with the filled shell cannot lead to deformation of the nucleus. The energy of the first excited state in the Zr^{92} and Zr^{94} isotopes is about 1 MeV, which also verifies the spherical symmetry of these nuclei. At the same time, the isotopic shift is different between the isotopes Zr^{90}, Zr^{92} and Zr^{94}. A similar situation is observed in one spectral line of molybdenum [8]. This indicates that the radius of the nucleus does not change uniformly, according to the $A^{1/3}$ law when various neutron shells are filled, but by a jump.

In conclusion, the author takes the opportunity to express his gratitude to A. R. Striganov for initiating and encouraging the present research.

Feb. 17, 1958

References

1. K. Murakawa and J. S. Ross, Phys. Rev. 83, 1272 (1951);
H. Arroe, Phys. Rev. 93, 94(1954);
L. A. Korostyleva: Opt. i Spektr. 3, 536(1957).
2. Brix, Van-Buttlar, Houtermans, and Kopfermann, Zs. f. Phys. 133, 192(1952).
3. E. Rasmussen and V. Middelboe, Kong. Dans. Vid. Selsk. Dan. Mat. Phys. 30, No. 13(1955).
4. S. Tolansky: High Resolution Spectroscopy. London, Methuen,(1947).
5. C. C. Kiess and H. K. Kiess, Bur. Stand. Jour. Res. 6, 621(1931).
6. R. H. Hughes, Phys. Rev. 105, No. 4(1957), p. 1260.
7. Wilets, Hill, and Ford, Phys. Rev. 91, 1488 (1953).
8. R. H. Hughes, Bull. Am. Phys. Soc., ser. II, 2(1957), p. 200.

TOM VI, Vyp. 1
VOL. VI, No.1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

Isotopic Analysis of the Absorption Spectrum of Copper Iodide

G. V. VEINBERG

INTRODUCTION

Spectroscopic isotope analysis has been widely used in recent years. The determination of isotopic composition has been made using atomic spectra in the majority of research. However, the isotopic shift is so very small for elements with medium atomic weight (it is 0.02 - 0.07 cm^{-1} [1] for Cu), that analysis by this method is difficult; consequently, it was decided to use molecular spectra for the isotopic analysis of copper.

Earlier, molecular spectra were successfully used to analyze lithium [2], nitrogen [3], carbon [4], polonium [5], boron [6] and hydrogen [7]. Electronic emission spectra in the visible were used in references [2-5] and infrared absorption spectra in references [6-7] for BF_3 and H_2O .

We used the absorption spectrum of CuI for the isotopic analysis of copper. The choice of CuI is explained, first, by iodines having only a single isotope, which simplifies the picture of the spectrum and, second, by the isotopic shift in the CuI spectrum being larger than in the spectra of other diatomic copper compounds because of the large atomic weight of iodine. Mulliken [8] observed the emission spectrum of copper iodide in 1925 and Ritschl [9] the absorption spectrum in 1927.

1. METHOD OF THE RESEARCH

The research was carried out on a DSF-3 spectrograph with a focal length of 400 cm and a first order plate factor of 4 Å/mm . An SVD-120 krypton-xenon tube was used as the source of the continuous spectrum. A quartz absorption cell with plane-parallel faces, into which the required quantity of CuI was inserted, was evacuated, sealed, and mounted in a parallel light beam. The cell was placed in a resistance furnace, which gave temperatures up to 1100° C ; because of the location of the resistance wire at the ends of the furnace, the temperature of the cell faces was maintained several degrees higher than in the center. The spectrum was photographed on "Spectral Type 3" photographic plates in the violet and green regions, and on panchromatic plates in the yellow. The exposure times, depending on the slit width, the temperature and the condition of the cell faces were from 10 sec to 15 min . Blackening marks were superposed on each plate by using a 9-step weakener.

In order to construct calibration graphs by which the determination of the isotopic composition could be made, CuI samples with a known isotopic composition of copper were produced. The separated isotopes of copper Cu^{63} and Cu^{65} , existing as Cu, Cu_2O and CuO , were converted into copper oxide, weighed and dissolved in nitric acid. Definite volumes of solutions of copper nitrate of known concentration were mixed with a solution of natural $Cu(NO_3)_2$. The copper iodide was obtained from the reaction

$$2Cu(NO_3)_2 + 4KI = 2CuI + 4KNO_3 + I_2$$

The excess iodine was titrated by a solution of sodium thiosulfate. The copper iodide, being precipitated in the sediment, was dried in a dessicator and was inserted in the cell as a powder.

The isotope concentrations in the standards prepared and their accuracy of preparation are indicated in Table 1. The low accuracy of the synthesis of the standards for the Cu^{65} concentrations, higher than in natural copper, is explained, first, by the small quantity of Cu^{65} and, second, by the composition of this isotope being known approximately only ($\sim$ 90% Cu^{65} and $\sim$10% Cu^{63}) .

Table 1

Number of Standard	Concentration of Cu^{65}, %	$\frac{Cu^{65}}{Cu^{63}}$	$\frac{\Delta(Cu^{65}/Cu^{63})}{Cu^{65}/Cu^{63}}$, %
1	1.0 ± 0.1	0.01	10
2	12.2 ± 0.3	0.139	3
3	22.0 ± 0.4	0.282	2
4*	30.5 ± 0.1	0.438	0.5
5	48 ± 2	0.91	4
6	72 ± 2	2.6	8
7	90 ± 2	9.0	20

* natural copper

2. INVESTIGATION OF THE ABSORPTION SPECTRUM OF CuI

In order to select the absorption band most convenient for the purposes of the analysis, we measured the isotopic shift for the strongest heads of the absorption band systems since similar measurements made by Mulliken were incomplete. Presented in Table 2 are the results of these measurements and their comparison with the results of Mulliken [8] and the values of the isotopic shift calculated by using the formula

$$(1)\quad \nu - \nu^{i} = (1-\rho)\,\omega_e''(v''+\tfrac{1}{2}) - 2\omega_e''x_e''(v''+\tfrac{1}{2})^2 - \omega_e'(v'+\tfrac{1}{2}) + 2\omega_e'x_e'(v'+\tfrac{1}{2})^2 \quad .$$

The values of the coefficients ω_e', $\omega_e'x_e'$, ω_e'' and $\omega_e''x_e''$ are taken from reference [9]. Spectrograms were made for the A, C, and D systems using the natural isotopic mixture of Cu^{63} and Cu^{65}, while the E system was photographed with separated isotopes as well. Greater accuracy was thus attainable in this latter case. By use of a Hartmann diaphragm, the spectra were placed side by side on the photographic plates.

The heads of the 0-2 and 0-3 bands of the E -system λ = 4090.8 and 4054.0 Å , for which the isotopic shifts are 0.77 and 1.02 Å , appeared to be most suitable for the analysis. These heads are convenient because the bands of other systems are not superposed thereon. A section of the spectrum near these bands for $Cu^{63}I$, $Cu^{65}I$ and natural CuI is shown in Figure 1.

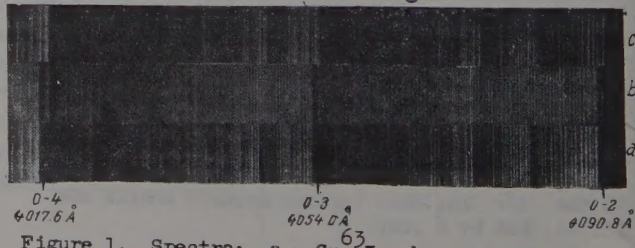


Figure 1. Spectra: a - $Cu^{63}I$, b - natural CuI , c - $Cu^{65}I$.

Table 2

Isotopic shifts of the band heads of CuI

A system

v'	v''	$\lambda_{Cu^{63}}$, Å measured	(ref. 8)	$\Delta\lambda$, Å measured	$\Delta\nu$, cm^{-1} measured	calculated	(ref.[8])	$\Delta\nu_{calc.} - \Delta\nu_{meas.}$
3	8	4886.1	4886.0	1.5	6.3	6.1	7.0	−0.2
0	4	4872.4	4872.8	2.0	8.4	7.6	8.1	−0.8
1	5	4889.5	4889.6	1.4	5.9	6.5	6.6	+0.6
0	3	4918.9	4919.1	1.1	4.6	5.7	7.3	+1.1
1	4	4936.0	4935.6	1.1	4.5	4.9	4.7	+0.4
0	2	4968.0	4968.3	1.0	4.0	3.8	3.7	−0.2
0	1	5019.0	5019.7	0.5	2.0	1.8	—	−0.2
1	2	5036.0	5034.6	0.6	2.4	1.1	—	−1.3
0	0	5072.3	5072.8	—	—	— 0.3	—	—
2	2	5101.3	5101.9	−0.3	−1.1	— 1.5	—	−0.4
1	0	5141.4	5141.1	−0.8	— 3.0	— 3.1	—	—
2	1	5156.7	5155.8	−1.4	— 5.3	— 3.6	—	+1.7
2	0	5211.5	5212.2	−1.5	— 5.5	— 5.7	— 5.4	−0.2
3	1	5225.6	5226.1	−1.4	— 5.1	— 6.2	— 6.6	−1.1
3	0	5283.3	5283.8	−2.4	— 8.6	— 8.0	— 7.2	+0.6
4	1	5297.3	5297.5	−2.5	— 8.9	— 8.4	— 8.5	+0.5
5	1	5370.0	—	−3.4	−11.8	−11.6	−11.5	+0.2
				C system				
0	2	4481.1	4482.0	1.0	5.0	4.5	—	−0.5
1	3	4489.4	4489.8	0.9	4.5	4.1	—	−0.4
0	1	4527.9	4527.9	0.5	2.4	3.2	—	+0.8
0	0	4575.2	4575.1	—	—	— 0.2	—	—
1	0	4630.9	4630.6	−0.5	−2.3	— 2.8	—	−0.5
2	1	4637.8	4638.0	−0.6	−2.8	— 3.2	—	−0.4
2	0	4687.8	4687.8	−1.2	−5.5	— 5.6	— 4.4	−0.1
3	1	4694.5	4694.0	−1.3	−5.9	— 5.9	— 5.5	0.0
4	2	4701.3	4701.7	−1.3	−5.9	— 6.2	— 6.8	−0.3
3	0	4746.4	4745.9	−1.7	−7.6	— 8.2	−10.5	−0.6
4	1	4752.4	4752.6	−1.9	−8.4	— 8.5	— 7.7	−0.1
5	2	4759.1	4759.3	−2.1	−9.3	— 8.8	— 8.3	+0.5
6	3	4765.8	—	−1.9	−8.4	— 9.0	— 7.8	−0.6
				D system				
0	3	4243.2	—	1.3	7.2	6.1	—	−1.1
0	2	4279.9	4281.9	1.0	5.5	4.1	—	−1.4
0	1	4319.9	4320.0	0.3	1.6	2.0	—	+0.4
0	0	4360.9	4359.9	—	—	— 0.3	—	—
1	0	4410.4	4410.8	−0.5	−2.7	— 3.0	—	−0.3
2	0	4461.3	4462.2	−1.1	−5.5	— 5.6	−5.7	−0.1
3	1	4471.7	4471.6	−1.0	−5.0	— 6.1	—	−1.1
3	0	4515.6	4514.8	−1.5	−7.3	— 8.3	−7.1	−1.0
				E system				
0	9	3850.5	3850.8*	2.84	19.2	19.4	—	+0.2
1	10	3858.8	3858.8*	2.78	18.7	18.6	—	−0.1
2	11	3866.8	3866.8*	2.57	17.2	17.9	—	+0.7
3	12	3875.0	3874.9*	2.45	16.4	17.1	—	+0.7
0	8	3882.5	3882.4*	2.64	17.4	17.4	—	0.0
1	9	3890.3	3890.3*	2.45	16.2	16.6	—	+0.4
2	10	3898.0	3898.0*	2.45	16.2	15.9	—	−0.3
3	11	3905.9	3906.0*	2.44	16.0	15.2	—	−0.8
0	7	3915.0	3915.3*	2.36	15.4	15.3	—	−0.1
1	8	3922.5	3922.6*	2.33	15.2	14.6	—	−0.6
2	9	3930.3	3930.4*	2.12	13.8	14.0	—	+0.2
3	10	3938.7	3938.1*	2.06	13.3	12.3	—	0.0
0	6	3948.9	3948.3*	1.98	12.7	13.2	—	+0.5
1	7	3955.7	3955.8*	1.90	12.1	12.6	—	+0.5
2	8	3963.2	3963.3*	1.84	11.7	12.0	—	+0.3
0	5	3982.4	3982.5*	1.74	11.0	11.0	—	0.0
1	6	3989.6	3989.7*	1.71	10.8	10.5	—	−0.3
0	4	4017.6	4017.5	1.42	8.8	8.9	—	+0.1
1	5	4024.8	4025.0	1.42	8.6	8.3	—	−0.3
2	6	4032.1	4032.3	1.16	7.2	7.8	—	+0.6
0	3	4054.0	4054.2	1.02	6.2	6.7	—	+0.5
1	4	4060.9	4061.3	0.93	5.7	6.2	—	+0.5
0	2	4090.8	4091.3	0.77	4.6	4.4	—	−0.2
2	4	4104.2	4105.0	0.52	3.1	3.8	—	+0.7
3	5	4112.3	4112.3	0.51	3.0	3.5	—	+0.5
0	1	4129.2	4129.4	0.32	1.9	2.2	5.5	+0.3
1	2	4135.9	4135.8	0.32	1.9	1.7	3.9	−0.2
2	3	4142.2	4142.2	0.28	1.6	1.3	—	−0.3
0	0	4168.0	4168.5	0.05	0.3	— 0.2	—	−0.5
1	1	4174.4	4174.6	−0.11	— 0.6	— 0.6	—	0.0
1	0	4214.4	4214.6	−0.51	— 2.9	— 2.9	—	0.0
2	1	4222.0	4221.0	—	—	— 3.2	—	—
3	2	4228.3	4227.0	−0.54	— 3.2	— 3.6	— 3.4	−0.4
2	0	4261.7	4261.7	−1.04	— 5.7	— 5.6	— 5.5	+0.1
3	0	4309.9	4309.6	−1.64	— 8.5	— 8.0	— 7.8	+0.5
4	1	4314.5	4315.4	−1.83	— 9.2	— 8.5	— 7.3	+0.7
4	0	4358.5	4358.3	−1.85	−10.5	−10.8	−11.3	+0.3

* Wavelengths taken from reference [9].

In addition to the investigation of the vibrational structure of the spectrum which only made the results of references [8-9] more precise, we studied the rotational structure of the bands selected for the analysis, which had not been observed earlier because of the inadequate resolving power of the apparatus used. We detected two series of lines describable by the formula

$$\nu = \nu_0 + am + bm^2 \qquad (2)$$

where the coefficients ν_0 and a depend on the numbering of the lines. The line closest to the edge of the band is taken as the origin. This line is not resolved and is found by extrapolation. The possibility of such an extrapolation is confirmed by the good agreement between the measured and calculated wave numbers of the heads of the bands (see Table 3). Under such numbering, the coefficient a in (2) is zero, and $\nu_0 = \nu_{edge}$ and the formulas for the wave numbers of the rotational lines are the following:

For the band with the head at 4054.0 Å

$$\nu = 24667.3 + 0.0086\ m^2 \qquad (3)$$

For the band with the head at 4090.8 Å

$$\nu = 24443.0 + 0.0083\ m^2 \qquad (4)$$

Table 3

λ_{head}	ν_{head} measured	calculated
4090.8	24443.1	24443.0
4054.0	24666.8	24667.3

Fifty lines of the 0-2 band and 120 lines of the 0-3 band were measured. The discrepancies between the measured wave numbers and those calculated using (3) and (4) did not exceed 0.3 cm^{-1}.

The determination of the actual values of the rotational quantum numbers is impossible in this case since the zero interval is in the unresolved part of the band, and a Q -branch is lacking. However, the fact that a systematic discrepancy between the measured isotopic shifts for the band heads and the calculated shifts made for the zero lines is not observed permits the statement that the head is formed for small values of the rotational quantum number. Rotational lines of the adjacent bands which have large quantum numbers are superposed on the band heads. Consequently, the band heads have a complex shape and their contours can alter substantially as the experimental conditions are varied.

3. SELECTION OF THE CONDITIONS FOR THE ISOTOPIC ANALYSIS

In order to make the analysis, 6 mg of CuI (2 mg of Cu) was placed in a cell 10 cm long and 1.5 cm in diameter. In this case, the optical densities to be measured were in the range 0.5-1.0 at a temperature of 900-1000° C, which guaranteed adequate accuracy of the absorption measurements.

Since copper isotopes are similar in physical properties, the ratio of the optical densities, due to the individual isotopes, must be independent of the experimental conditions and should equal the

ratio of their concentrations. If the optical density due to the first isotope (Cu^{63}) is $D_1 = \log(I_{01}/I_0)$ and the optical density, due to the second isotope (Cu^{65}) is $D_2 = \log(I_{02}/I_0)$ (see Fig. 2a), then

$$D_1/D_2 = C_1/C_2 \tag{5}$$

i.e., the calibration graph must be a line passing through the origin at 45 degrees to the axes. The superposition of a rotational line of the second isotope on the band head of one isotope leads to the violation of (5). If it is assumed that a rotational line of the one isotope is superposed exactly on the band head of the other (see Fig. 2b) then, as is easy to show,

$$D_1/D_2 = (C_1 + aC_2)/(C_2 + bC_1) \tag{6}$$

where the coefficients a and b have the following meaning: $a = D_1/D_2$ for $C_2 = 0$; i.e., a is the ratio of the optical density of the rotational line of the second isotope imposed on the band head of the first isotope to the density of the band head of the same isotope. Similarly, $b = D_2/D_1$ for $C_2 = 0$, i.e., b is the ratio of the optical density of the rotational line of the first isotope superposed on the band head of the second isotope to the optical density of the band head of this same isotope. The form of the function (6) is shown in Figure 3 on a logarithmic scale for various values of the corrections a and b. The graph should approach a line passing through the origin at a 45 degree angle as a and b decrease.

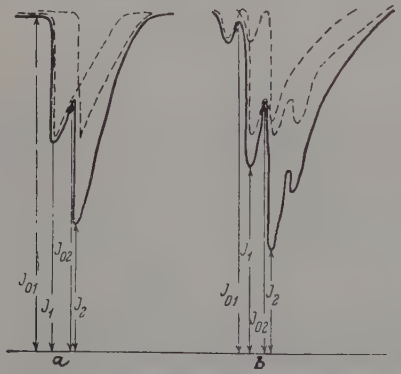


Figure 2. Sum of the absorption of two isotopes without taking the rotational structure of the band heads into account (a), and taking the rotational structure into account (b).

The magnitudes of the coefficients a and b depend substantially on the width of the spectrograph slit and the temperature of the absorbing vapors. Shown in Figure 4 is the optical density of the band head, the rotational line, and their ratio as a function of the width of the spectrograph slit, for the 4054.0 Å head. It is seen from Figure 4 that the correction $b = D_2/D_1$ decreases significantly as the slit increases to 0.8 mm. Broadening of the slit to more than 0.12 mm is not recommended since the resolution of the band heads for the two isotopes is hereby degraded. Shown in Figure 5 are calibration curves for the 4054.0 Å head for 0.06 and 0.10 mm slits. As should be expected, the graph in the latter case approximates a line passing through the origin at a 45 degree angle to the axes.

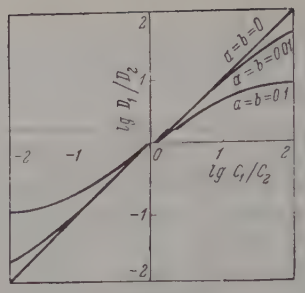


Figure 3.

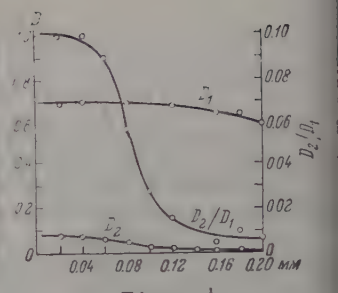


Figure 4.

Figure 3. Theoretical calibration curves taking account of superposition of a rotational line of one isotope on a band head of the other isotope.

Figure 4. Optical density of a band head, a rotational line, and their ratio as a function of slit width.

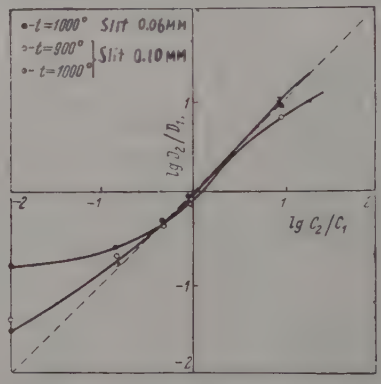


Figure 5. Shift of the calibration curve for a change in slit width, for λ 4050.0 Å.

The second factor to influence the magnitude of the corrections a and b is the temperature. As the temperature increases, the population of the higher rotational levels increases and, therefore, the optical densities of the rotational lines, which, as mentioned above, have considerably larger quantum numbers than the heads, increase more rapidly with temperature. Second, as the temperature increases, the contour of the rotational line changes both because of the Doppler effect and also because of the pressure increase in the cell, which should affect the optical density of the head and the lines differently. A change in the ratio of the optical density of the lines and heads is shown in Figure 6 for a change in the temperature, for slits of different widths. The change in the corrections a and b with temperature should lead to a shift of the calibration curves as the temperature changes (see Fig. 7), wherein the influence of the temperature is particularly large in the range of small concentrations where the corrections a and b play a decisive part. Hence, the temperature should be maintained constant to 20-30° accuracy for operation with narrow slits. However, not only the magnitude of the correction is less as the slit width is increased to 0.10 mm, but also changes in conditions affect the behavior of the calibration curves to a lesser extent. Thus, points corresponding to temperatures of 900° and 1000° in Figure 5 are in agreement within the limits of measurement accuracy.

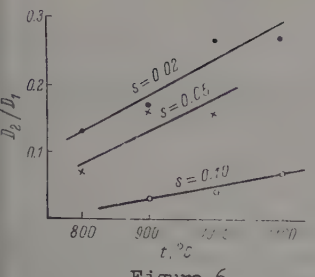


Figure 6.

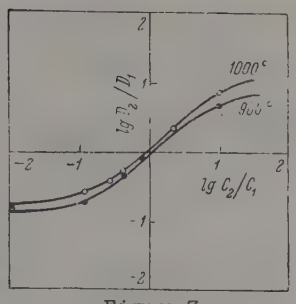


Figure 7.

Figure 6. Temperature dependence of the coefficient b for various slit widths.

Figure 7. Shift in the calibration curve for a change in temperature, for λ 4054.0 Å, with a 0.06 mm slit width.

4. DISCUSSION OF RESULTS

The accuracy of determining the isotopic composition is determined, first, by the accuracy of measuring the optical densities and, second, by the slope of the calibration curve. In its turn, the accuracy of measuring the optical density depends on the magnitude of the absorption and on the constancy of the photographic material. As a computation showed, the maximum accuracy for the plates we used, with $\gamma = 2$, is achieved for an optical density of $\log I_0/I \sim 0.5$ when working in the normal blackening range. The reproducibility of the measurements of D_1/D_2 in the range where $D_1/D_2 = 4 - 0.25$ is 4-5%. However, an incorrect choice of the exposure time, just as working with too large or too small an absorption, can increase the measurement error in this range to 10% and higher. The calibration curve has a slope close to 45 degrees in the 20 - 80% range of concentration, i.e., for $C_1/C_2 = 4 - 0.25$; consequently, the accuracy of determining the concentration in this range by using the graph, is equal to the accuracy of measuring the ratio D_1/D_2, i.e., is 4 - 5 %. The slope of the graph depends substantially on the slit width (see fig. 5) in the $C_1/C_2 = 0.1 - 0.05$ range. Thus, an error of 25% in the determination of the concentration corresponds to an error of 5% in the measurement of D_1/D_2 for an 0.06 mm slit. The slope of the graph is so small in the $D_1/D_2 = 0.01$ range that a measurement of the ratio of the concentrations is impossible. However, the slope of the graph is considerably larger in this region for wider slits and, despite the low accuracy in measuring D_1/D_2 because of the comparability of the absorption D_1 to the fluctuations of the plate, the accuracy of measuring the ratio of the concentrations is about equal to 50%.

When operating with slits of about 0.10 mm width, the calibration curve is so very close to the line $D_1/D_2 = C_1/C_2$ that an absorption analysis can be made in the medium concentration range without using standards. Hence, the error in determining the isotopic composition for 20 - 80% concentrations does not exceed the reproducibility of the measurements. The departure of the calibration graph from the line corresponding to (5) is beyond the limits of reproducing the measurements of D_1/D_2 for 10 - 20% concentrations and the error in the measurements directly in terms of the absorption ratio is 25%. Hence, the analysis without standards can be considered as semi-quantitative in this range.

As a result of studying the conditions of the analysis, it was clarified that not only is it possible but also useful to work with slits considerably wider than the normal slits. Hence, the resolving power of the instrument was reduced; consequently, simpler instruments with lower resolving powers and dispersions can successfully be used in the analysis. The calibration graphs, obtained on a KSA spectrograph with glass optics using a 0.10 mm slit width, are similar to graphs obtained on a DSF-3 instrument with a 0.15 mm slit. Such instruments as the DS-1, ISP-51 with an F = 80 cm camera lens and similar ones are completely suitable for the research.

I would like to express my deep appreciation to A. N. Zaidel' for supervision and constant interest in the research and to V. S. Zolotarev for providing the separated copper isotopes required for the research.

March 5, 1958

References

1. S. Wagner, Zs. f. Phys. 141, 122(1955).
2. Nakamura, Nature 128, 759(1931).
3. A. I. Gorbunov, P. A. Zagorets: Zh. Fiz. Khim., 29, 1442(1955).
4. R. E. Ferguson and H. P. Broida, anal. chem. 29, 1442(1955).
5. D. J. Hunt and G. Pish, J. Opt. Soc. Amer. 46, 87(1956).
6. Mal'tsev, Moskvina and Tatevskii: Materials of the X All-Union Conference on Spectroscopy. L'vov Univ. Press, 1, 472(1957).
7. J. Gaunt, The Analyst 79, 580(1954).
8. R. S. Mulliken, Phys. Rev. 26, 1(1925).
9. Ritschl, Zs. f. Phys. 42, 172(1927).

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January, 1959

Time Resolved Spectra of the Radiation From a Spark Discharge in Inert Gases

M. P. VANIUKOV, A. A. MAK, and V. R. MURATOV

Abstract: The light intensity spectra of a pulsed discharge in atmospheres of argon, krypton, and xenon were investigated in the 2500-5500 Å region of the spectrum, at a gas pressure of 3.5 times the atmospheric pressure. A spectrophotometric setup, having about 5×10^{-8} sec. resolution, was used.

INTRODUCTION

The measurement of the spectral density in the visible portion of the spectrum of the bright channel of a pulsed discharge in the heavy inert gases, at a high pressure and a large current density, has shown that the temperature of the discharge channel reaches 20,000-30,000° K . [1] Therefore it was interesting to investigate the variations with respect to time, of radiation spectra of such a discharge in the ultraviolet region of the spectrum also, because the intense spark lines of inert gases are located in that region. The arc lines, as was shown in [2], unlike the spark lines, characterize mainly the condition of the channel envelope.

The time resolved spectra of the light from a high pressure spherical pulsed discharge lamp in the 2500-5500 Å region of the spectrum for various values of the discharge network components, are described in this work.

CALIBRATION OF THE APPARATUS

The time resolved spectra were obtained using a photoelectric setup previously developed [2]. A monochromator mounted in the Ebert-Fastie manner was used, with a 320 mm mirror objective, an 1800 mm focal length, and a 90 X 110 mm diffraction grating, having 600 grooves/mm . The relative spectral sensitivity of the apparatus was determined using a ribbon filament standard lamp with a quartz window, having a brightness temperature of 2000° C [3]. In order to decrease the amount of scattered light as the sensitivity of the apparatus in the 2500-3000 Å wave-length region was being determined, a pre-graduated gas filter made from a mixture of chlorine and bromine and a UF S-1 glass filter were placed in front of the input slit of the monochromator, which cut out the radiation of wavelengths greater than 3000 Å . The absolute (energy) scale for the spectra was determined at 4140 Å wavelength using a filament lamp, whose spectral energy density of the light intensity was known for this wavelength. The effective spectral width of the slits of the monochromator varied during the experiment, depending on the intensity of the radiation, from 2 to 20 Å .

RESULTS OF THE MEASUREMENTS

The instantaneous values of the light intensity from the pulsed lamps were measured at various times after the beginning of the discharge, for different values of the operating voltage U , capacity C , and inductance L in the discharge circuit. Gas pressures in the lamps were 3.5 atmospheres, with electrode spacings of 10 mm . The earliest moment possible after the start of the discharge for which a spectrum photograph could be taken, corresponded as a rule to the maximum value of light intensity.

The results of the measurements of spectral density of the light intensity i_λ from argon-filled lamps, are shown in Figures 1 and 2. As seen from those figures, an early and intense development of the line spectrum is observed, especially in the 3600 Å wave-length region, as the value of the working capacitor is decreased.

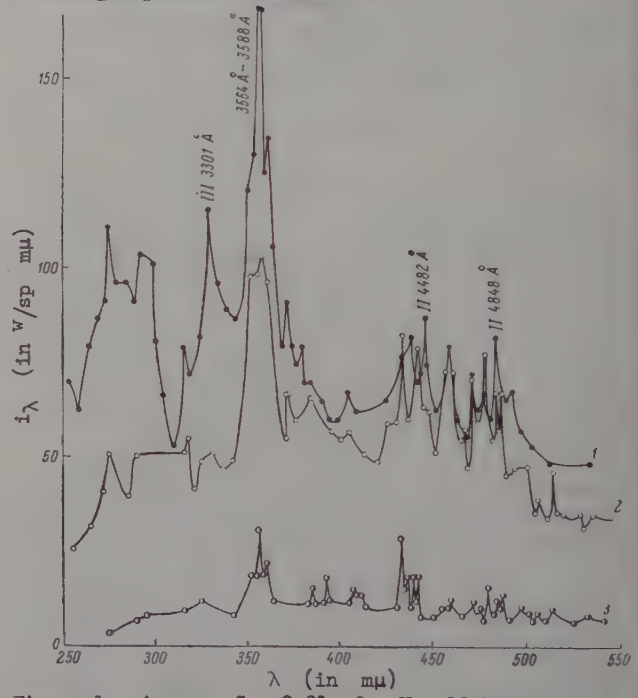


Figure 1. Argon. C = 0.01 μf ; U = 10 kV ; L = 0.1 μH
t (in μsec): 1 - 0.3; 2 - 0.4; 3 - 1.2

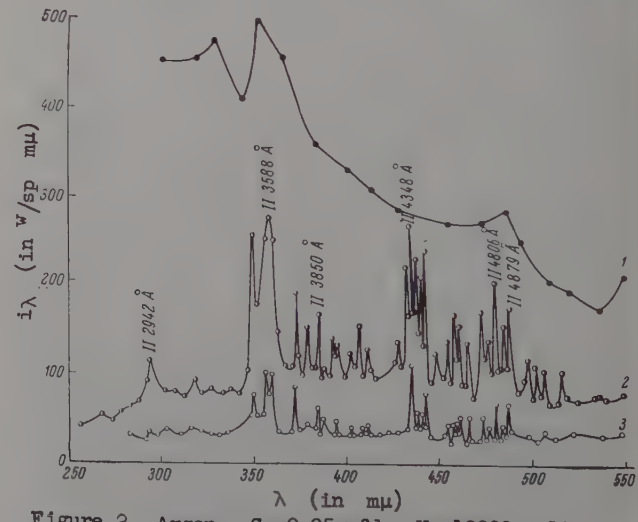


Figure 2. Argon. C--0.05 mfd; V--10000 volts;
L--0.1 microhenry t(in microseconds):
1--0.4; 2-1.2; 3-2.1

The radiation spectra of discharges in krypton at various values of the discharge network inductance and operating voltage, are shown in Figs. 3-5.(1)

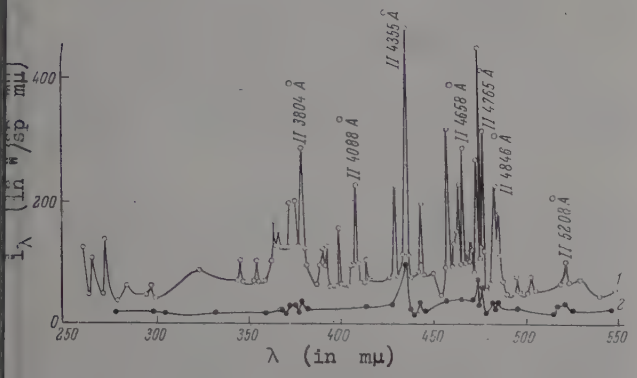


Figure 3. Krypton. C--0.05 mfd; V--10000 volts; L--25 microhenry t(in microseconds): 1-2; 2-3.3

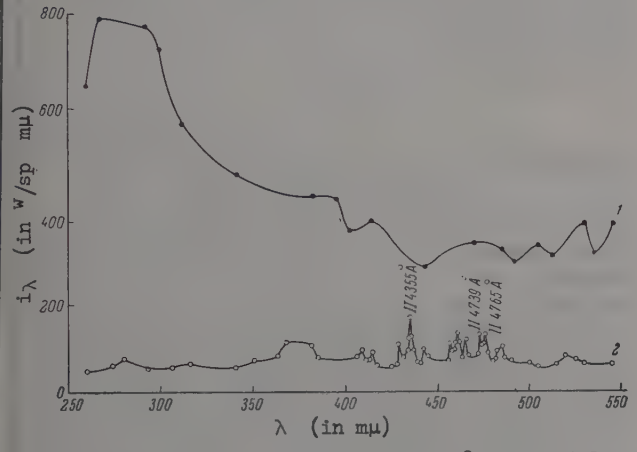


Figure 4. Krypton C--0.05 mfd. V--8KV; L--0.1 microhenry t(in microseconds): 1-0.4; 2-1.6

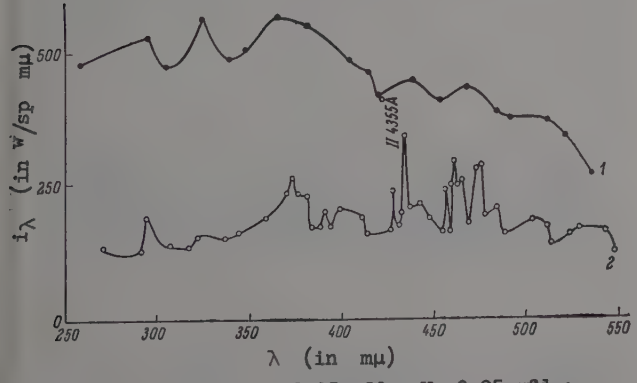


Figure 5. Krypton C--0.05 mfd. V--0.05 mfd.; V--10KV; L--0.1 microhenry t(in microseconds); 1-0.8; 2-1.6

(1) The spectrum for the instant of time t=0.8 microseconds, given in Fig. 5, does not correspond to the maximum value of light intensity.

The plot of i_λ for discharges in xenon at various operating conditions are given in Fig. 6 to 9.

The study of spectra, given in Figs. 1 through 9, allows us to draw certain conclusions about the general nature of radiation in high-temperature spark discharges. The value of the inductance of the discharge network has a large effect on the character of the radiation. An increase in inductance leads to a general decrease in intensity of continuous radiation, and as a result, line radiation becomes more pronounced.

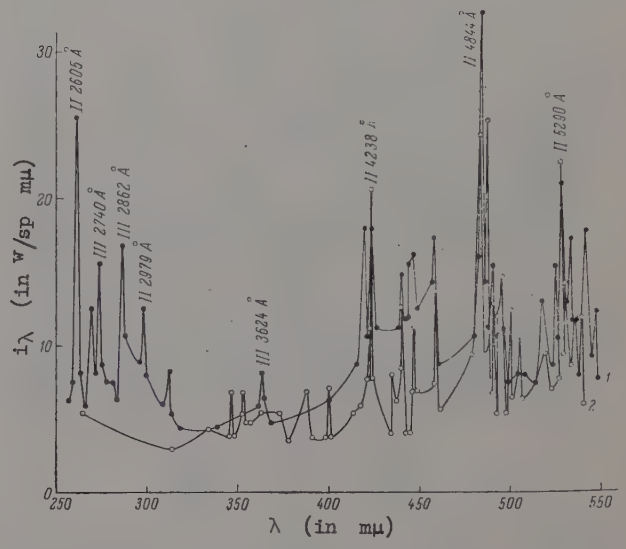


Figure 6. Xenon C--0.05 mfd; V--12KV; L--25 microhenry t(in microseconds); 1-3.3; 2-7.1

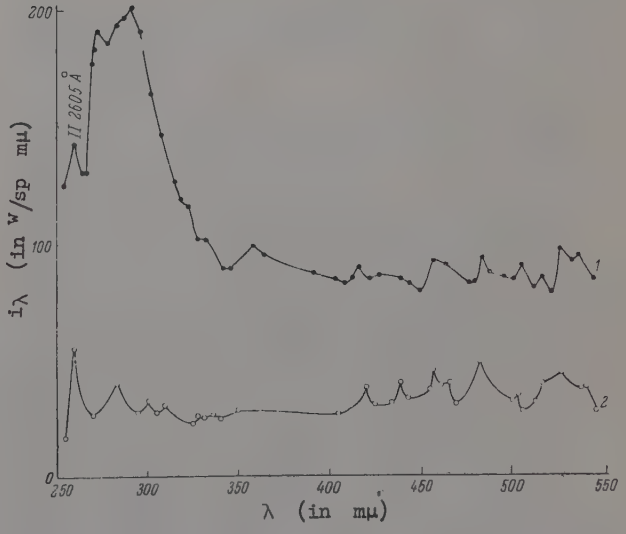


Figure 7. Xenon C--0.01 mfd; V--12KV; L-0.1 microhenry t(in microseconds); 1-0.3; 2-1.2

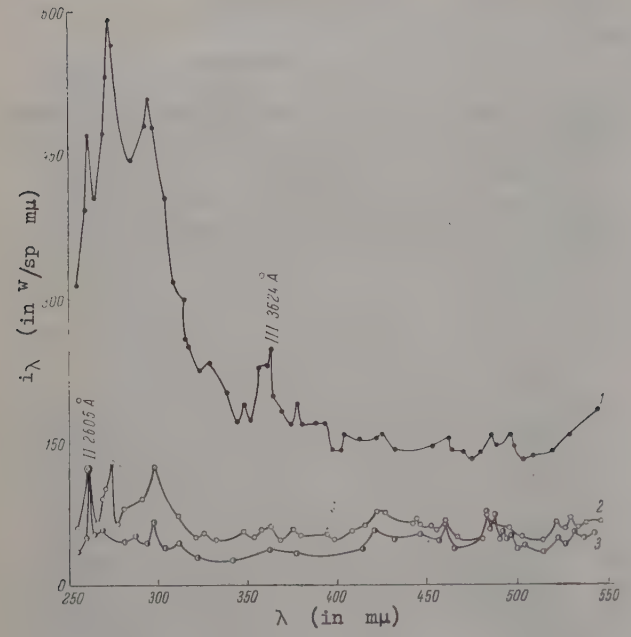


Figure 8. Xenon C--0.05 mfd; V--5KV; L--0.1 microhenry t(in microseconds): 1-0.3; 2-0.8; 3-1.2

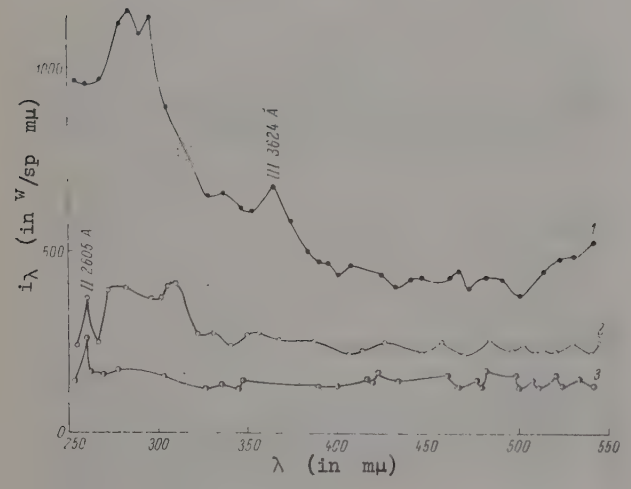


Figure 9. Xenon C--0.05 mfd; V--12KV; L--0.1 microhenry t(in microseconds): 1-0.8; 2-1.6; 3-2.1

Continuous radiation and line radiation of doubly ionized atoms appear first in the process of the development of discharge. The radiation of singly ionized atoms then appears in the latter's place, and finally it too dies out, although more slowly than the continuous radiation.

The distribution of continuous radiation by wave-lengths is quite different from the distribution of black-body radiation, displaying little dependence on the wavelength. This may be explained by the fact that at the instants of time we investigated, the channel of the discharge has become transparent and the temperature through its cross-section is not the same. The appearance of radiation maxima in various parts of the spectrum may be attributed to the unresolved groups of lines. Thus for instance, the radiation maximum in the 2700-3000 Å region of the spectrum appearing in the early stage of discharge in xenon may be considered as due to the radiation of doubly ionized xenon atoms, appearing as very broad and therefore unresolved lines.

It is also interesting to note, that as the energy of the discharge is increased, the magnitude of the light intensity of the pulsed lamps rises proportionally with the square root of electric energy in the spark gap.

CONCLUSIONS

1. The time resolved spectra of radiation from high-temperature discharges in inert gases show that at an early stage of the discharge, when the light intensity of the discharge reaches a maximum value, a considerable concentration of doubly ionized atoms of the gas filling the lamp is formed in the discharge channel. This is especially noticeable in the case of discharges in xenon.

As the discharge channel cools off, doubly ionized atoms are quickly replaced by singly ionized ones. The line radiation from singly ionized atoms lasts longer than the continuous radiation.

2. The distribution throughout the spectrum of continuous radiation of the discharge channel shows, that the spectral intensity displays little dependence on the wavelength. This fact may be attributed, it seems, to the unequal temperatures in various parts of the channel, and also to the difference in absorption coefficients of the plasma for various regions of the spectrum.

References

1. M. P. Vaniukov, A. A. Mak, N. V. Parazinskaia: Optics and Spectroscopy, 1, No. 5, 642, 1956.
2. M. P. Vaniukov, L. D. Khazov: DAN USSR, 92, No. 3, 523, 1953.

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

On The Electronic Absorption Spectra Of The Aliphatic Polysulfides

T. K. REBANE

Abstract: An investigation has been made of the source of the red shift in the long wavelength absorption maximum in the electronic spectra of aliphatic polysulfides, as the length of the polysulfide chain increases. It is shown that this shift is due to a splitting of the 3p and 4s levels of the sulfur atoms in the polysulfide chain. A quantum mechanical calculation of this shift, using the method of molecular orbitals, gives satisfactory agreement with experiment.

INTRODUCTION

The ultraviolet absorption spectra of the organic polysulfides are characterized by a high sensitivity to the number of sulfur atoms in the polysulfide chain. Moreover, as the length of the chain increases, the absorption bands shift noticeably in the long wavelength direction. [1,2] Thus, in their optical behavior, the polysulfides recall the conjugated hydrocarbon polymers. On the basis of this analogy, attempts have been made to relate peculiarities of the ultraviolet spectra of the polysulfides to the effects of coupling the unshared electron pairs of the sulfur atoms. Up to now, however, the theory of the optical properties of the polysulfides has not been worked out. Hence, in this connection in the present article, a quantitive treatment of the electronic spectra of the aliphatic polysulfides has been made by using the simplest methods of quantum chemistry.

1. A BRIEF DESCRIPTION OF THE ELECTRON STRUCTURE OF THE POLYSULFIDE CHAIN

Consider the electronic ground state of the polysulfide chain R_1-S_1-S_2- ... S_n-R_2. Of the six valence electrons belonging to each sulfur atom in this chain two (the so-called 3 σ-electrons) take part in the formation of bonds with the nearest neighbors. Around each sulfur atom the four remaining valence electrons form two unshared pairs, one of which occupies the hybrid 3s-3p orbital (which we designate 3n), and the second pair occupies the non-hybrid 3p orbital. The hybrid 3n orbital is coplanar with the two 3 σ-bonding orbitals of the same sulfur atom, and the non-hybrid 3p orbital is perpendicular to the plane in which the 3 σ-bonding orbitals and the non-bonding 3n orbital lie.

Using the principle of maximum overlap of the bonding orbitals of neighboring atoms, it is possible to determine the approximate form of the dependence of the 3s-3p hybridization degrees of the 3 σ-bonding orbital, as well as of the non-bonding 3n orbital, on the angle α between the two bonds formed by the given sulfur atom. An appropriate calculation shows that the ratio of the contributions of 3p and 3s orbitals to the hybrid non-bonding 3n orbital is approximately equal to

$$f(\alpha)=\frac{1}{2}\left(\mathrm{tg}^2\frac{\alpha}{2}-1\right). \qquad (1)$$

Let us consider the geometry of the polysulfide chain to differ very little from that of fibrous sulfur, treated by Pauling, [3] where all S-S bonds have a length of 2.08A, all angles S - S - S are $\alpha = 106^\circ$, and where the planes of the bonds, formed by two neighboring sulfur atoms, meet in an angle $\beta = 76^\circ$.

When $\alpha = 106^\circ$, formula (1) shows that the contributions of 3s and 3p orbitals to the hybrid 3n orbit of the unshared pair of sulfur atoms in the polysulfide chain are 72 and 28%, respectively.

Hence it is clear that the electronic ground state of the polysulfide chain has lost the features which characterized the conjugate systems. Actually, all the energy levels formed from the unexcited atomic 3s and 3p levels of sulfur are now completely filled with electrons. At the same time, in conjugate systems, there are always unfilled energy levels formed from unexcited atomic levels (for example, from the 2p levels of the carbon atoms in conjugated hydrocarbons).

The result of this is that, in contrast to conjugated hydrocarbons, the electrons of the polysulfide chain may be excited into only those energy levels which are formed from excited levels of the sulfur atom. According to reference [4], the lowest excited states of an isolated sulfur atom have the following excitation energies:

$3s^23p^3\ 4s$	(^5S)	52624 см$^{-1}$
$3s^23p^3\ 4p$	(^5P)	63446 см$^{-1}$
$3s^23p^3\ 3d$	(^5D)	67878 см$^{-1}$.

Accordingly, the most easily excited transition in the sulfur atom is 3p-4s. The large excitation energy of the 3s-3p-transition in atomic sulfur (72,026 cm^{-1}) and the noticeably high preponderance of 3s character in the hybrid 3n orbits show that the non-bonding 3n electrons of the sulfurs take practically no part in the long wavelength absorption of light (of excitation energies less than 50,000 cm^{-1}).

Hence it follows that the unshared 3p electrons of sulfur are responsible for absorption at long wavelengths in the polysulfides. The electrons when excited make the transition into the free 4s levels of the polysulfide chain. In this manner we can regard the problem of the long wavelength absorption in a polysulfide chain as the problem of 2N "optical" electrons, occupying basically the states of non-bonding 3p orbitals of the sulfur atoms.

Finally we note that this statement of the problem implies neglect of the influence exerted on the long wavelength absorption spectra of the polysulfides by the interaction of the polysulfide chain with the radicals which are attached to it. In the case of the aliphatic radicals, neglect of this effect is justified and is supported by the small magnitude of the shift in the frequency of the long wavelength absorption maximum (from about 50,000 cm^{-1} for aliphatic monosulfide R_2S to 52,600 cm^{-1} for the 3p-4s transition in an isolated sulfur atom). In the case of aromatic polysulfides, it is not possible to neglect the interaction of the "optical" electrons of the polysulfide chain with the radicals attached to it (this follows from the experimental data supplied in reference [2]). We

will limit ourselves below to the case of aliphatic polysulfides.

2. THEORETICAL TREATMENT OF THE LONG WAVELENGTH ABSORPTION BAND IN ALIPHATIC POLYSULFIDES BY THE METHOD OF MOLECULAR ORBITALS

To handle the problem of the 2N "optical" electrons, described in the previous section, let us use the simplest variant of the molecular orbital method, the approximation of linear combinations of atomic orbitals, without taking into account the nonorthogonality integrals. In this approximation the molecular orbitals of the non-bonding 3p electrons of the polysulfide chain ψ_l^{3p} take the form

$$\psi_l^{3p} = \sum_{\gamma=1}^{N} c_{\gamma, l} \chi_\gamma^{3p} \quad (l = 1, 2, \ldots, N) \tag{2}$$

(where χ_γ^{3p} is the non-bonding 3p-orbital of the γth sulfur atom).

Analogously, the excited molecular orbitals of the 4s electrons of the polysulfide chain take the form

$$\psi_m^{4s} = \sum_{\gamma=1}^{N} d_{\gamma, m} \chi_\gamma^{4s} \quad (m = 1, 2, \ldots, N). \tag{3}$$

The coefficients $c_{\gamma, l}$ and $d_{\gamma, l}$ are defined by the usual finite-difference equations for the molecular orbital method

$$\beta^{3p} c_{\gamma-1, l} + (\alpha^{3p} - E_l^{3p}) c_{\gamma, l} + \beta^{3p} c_{\gamma+1, l} = 0, \tag{4a}$$

$$\beta^{4s} d_{\gamma-1, m} + (\alpha^{4s} - E_m^{4s}) d_{\gamma, m} + \beta^{4s} d_{\gamma+1, m} = 0. \tag{4b}$$

(where γ, l and m = 1,2,....,N). Here α^{3p}, β^{3p}, α^{4s} and β^{4s} represent the "coulomb" and "resonance" integrals, familiar in the theory of molecular orbitals, and computed with the χ^{3p} and χ^{4s} atomic orbitals. The solutions of equations (4a) and (4b) have the same form:

$$c_{\gamma, l} = d_{\gamma, l} = \sqrt{\frac{2}{N+1}} \sin \frac{\gamma l \pi}{N+1} \tag{5}$$

The energy levels of the ψ_l^{3p} and ψ_m^{4s} molecular orbitals are given by the formulas:

$$E_l^{3p} = \alpha^{3p} + 2\beta^{3p} \cos \frac{l\pi}{N+1}, \tag{6a}$$

$$E_m^{4s} = \alpha^{4s} + 2\beta^{4s} \cos \frac{m\pi}{N+1}. \tag{6b}$$

In the unexcited electronic state of the polysulfide chain all the energy levels of the non-bonding 3p electrons are completely occupied, and all the levels of the 4s electrons are empty. The smallest excitation energy ΔE_{min} is required for an electron transition from the highest occupied 3p level E_N^{3p} to the lowest unoccupied 4s level E_1^{4s}.

From equations (6a) and (6b) we find:

$$\Delta E_{min}(N) = E_1^{4s} - E_N^{3p} = \alpha^{4s} - \alpha^{3p} + 2(\beta^{4s} + \beta^{3p}) \cos \frac{\pi}{N+1}. \tag{7}$$

Computation of the integrals α^{3p}, β^{3p}, α^{4s} and β^{4s} in the last formula presents great difficulty because of the absence of sufficiently accurate information about the form of the effective one-electron Hamiltonian for the polysulfide chain, as well as about the form of the 3p and 4s wave functions of the sulfur atoms. Therefore we are forced to turn to an empirical method to define the coefficients of formula (7). Setting N = 1 and 2 successively in formula (7) we get:

$$\Delta E_{min}(1) = \alpha^{4s} - \alpha^{3p}, \tag{8}$$

$$\Delta E_{min}(2) = \alpha^{4s} - \alpha^{3p} + \beta^{4s} + \beta^{3p}. \tag{9}$$

The long wavelength absorption maxima of the aliphatic polysulfides are characterized by the excitation energies presented in the second column of the table. In the same column are given references to the literature. A comparison of formulas (8) and (9) with the experimental values of ΔE_{min} [1] and ΔE_{min} [2] from the table allows one to define the coefficients in formula (7), which now takes the form

$$\Delta E_{min}(N) = \left(50\,000 - 20\,600 \cos \frac{\pi}{N+1}\right) \text{cm}^{-1}. \tag{10}$$

The values calculated from formula (10) for the excitation energies of the long wavelength electron transition in the polysulfide R_2S_N, listed in the third column of the table, agree satisfactorily with existing experimental data.

POSITION OF THE LONG WAVELENGTH ABSORPTION MAXIMA FOR THE ALIPHATIC POLYSULFIDES

N	Experiment		Theory
1	50,000 cm^{-1}	[1]	50,000 cm^{-1}
2	39,700	[1]	39,700
3	39,800	[1]	35,400
4	33,300	[1]	33,300
6	30,800	[2]	31,400
	--		29,400

It is necessary to take account of the uncertainty in the observed position of the long wavelength absorption maximum in the trisulfides. The authors [1] observe that the coincidence of the position of the maxima in the long wavelength absorption of the di- and trisulfides is random in nature. The long wavelength absorption band of the trisulfides is very wide, and the position of its shallow maximum (λ_{max} = 2510 Å, log ϵ = 3.22) is strongly perturbed by the intense short wavelength absorption band (λ_{max} = 2130 Å, log ϵ = 3.87). At the same time there is a strongly marked red shift, relative to the disulphides, of the edge of the long wavelength absorption band in the trisulfides, a shift of around 3500 cm^{-1} at an intensity level of $1.0 \leq \log \epsilon \leq 2.0$. The latter value is close to the theoretical value

for the shift in the absorption maximum of the trisulfides relative to the disulfides (4300 cm^{-1}).

Hence the simple semi-empirical method of molecular orbitals used here gives a correct description of the long wavelength shift in the electronic absorption spectra of the aliphatic polysulfides as a function of the increasing length of the polysulfide chain.

The author extends deep thanks to E. N. Gur'ianova for valuable comments on the manuscript.

March 17, 1958

REFERENCES

1. J. E. Baer, M. Carmack. J. Am. Chem. Soc., 71, 1215, 1949.
2. H. P. Koch. J. Chem. Soc., 394, 1949.
3. L. Pauling. Proc. Nat. Acad. Sci., 35, 495, 1949.
4. C. E. Moore. Atomic Energy Levels. Washington, 1949.

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

On the Breakdown of the Kramers-Kronig Dispersion Relations in Molecular Crystals at Various Temperatures

M. S. BRODIN, A. F. PRIKHOT'KO AND M. S. SOSKIN

Abstract; An experimental investigation has been made of the Kramers-Kronig dispersion relations for anthracene, 1, 2-benzanthracene, stilbene, and tolane at temperatures of 290, 80, and 20°K. The results of the investigation show that in the majority of the cases investigated, these relations are seriously violated; the violation is greatest at the lowest temperatures.

INTRODUCTION

The phenomena of dispersion and of absorption of light has received markedly less experimental and theoretical study in crystals than in gases. The general dispersion relations, which give an integral relation between the index of refraction and the coefficient of absorption of a substance, are the phenomenological formulae due to Kramers and Kronig [1]. They are a consequence of Maxwell's equations and should hold whenever the latter do.

Regardless of the fact that these formulae were presented more than thirty years ago, (1927), they have not been investigated experimentally for crystals in a sufficient number of cases. At present there is a well-defined literature of simultaneous studies of dispersion and absorption in crystals. For certain substances, at room temperature, the Kramers-Kronig relations seem to hold [2], [3]. For all these substances, however, deviations between theory and experiment were observed at low temperatures; hence the purpose of the present work is to study the dispersion relations in greater detail for a large number of materials at various temperatures. We have chosen to investigate the following molecular crystals: anthracene, 1, 2-benzathracene, stilbene, and tolane, all of which strongly absorb light.

THE KRAMERS-KRONIG DISPERSION RELATIONS FOR OPTICAL QUANTITIES

The Kramers-Kronig equations give a universal relation between the real and the imaginary parts of the dielectric constant $\epsilon(\omega) = \epsilon'(\omega) + j\epsilon''(\omega)$, defined from the Maxwell equation $\vec{D} = \epsilon\vec{E}$ (see reference [1]).

$$\varepsilon'(\omega) - 1 = \frac{2}{\pi}\int_0^\infty \frac{x\varepsilon''(x)}{x^2 - \omega^2}\,dx, \tag{1}$$

$$\varepsilon''(\omega) = -\frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\varepsilon'(x) - 1}{x - \omega}\,dx. \tag{2}$$

Here x, the variable of integration (frequency), takes on all real values, and the principal values of the integrals are to be taken. For the case of an isotropic media ϵ' and ϵ'' are tensors. As is well-known, $\epsilon(\omega) = n^2(\omega)$, where $n(\omega) = \mu(\omega) + j\chi(\omega)$ is the complex index of refraction; μ and the coefficient of absorption χ, which we get from equation (1), can be written in the following form for optical quantities:

$$\mu^2(\omega) - \chi^2(\omega) - 1 = \frac{4}{\pi}\int_0^\infty \frac{x\mu(x)\chi(x)}{x^2 - \omega^2}\,dx. \tag{3}$$

Generally speaking the form of equation (3) is true for isotropic media. For an isotropic media it has the same form for those directions of polarization of the incident light which, from symmetry considerations, coincide at all frequencies with the principal axes of both the ϵ' and the ϵ'' tensors. In the case of monoclinic crystals these axes are the monoclinic axes, and for crystals of higher symmetry, all three principal axes. Formula (2) gives a reciprocal relation which is less amenable to experimental investigation.

The integral equation (3) cannot be solved in simple form to give the dependence of μ on χ, and therefore, in order to make comparisons with experiment, it is necessary to make use of the curve $\chi\mu$, which for purposes of calculation may be conveniently approximated by a sum of Gaussian terms $A_i e^{-(\nu - \nu_i)^2/\delta_i^2}$. Here A_i is the magnitude of the i^{th} maximum, ν_i is its frequency, δ_i is a quantity proportional to its half-width, and ν is the frequency. Then as was shown by E. I. Rashba, formula (3) takes the form:

$$\mu^2(\nu) = 1 + \chi^2(\nu) - \frac{4}{\sqrt{\pi}}\sum_i A_i w\left(\frac{\nu - \nu_i}{\delta_i}\right), \tag{4}$$

where $\omega(z) = e^{-x^2}\int_0^z e^{x^2}dx$. Since the function $\omega(z)$ has been tabulated, calculation with this formula is greatly facilitated.

EXPERIMENTAL SECTION

The experimental data on the absorption and dispersion of light in monocrystalline anthracene, [5], [6] stilbene and tolane [7] have been published earlier. The data for 1, 2-benzanthracene are published in the present paper. In all cases measurements were made on thin monocrystalline slabs produced by sublimation from the pure substance. They were highly perfect films, uniform in thickness, with well-developed flat surfaces. Polarized light was used for the measurements. The dispersion curves were measured by the interferometer method with the help of a Jamin interferometer. The absorption curves were measured by the methods of photographic and photoelectric photometry.

For purposes of investigating the dispersion relations, χ and μ were calculated from the usual formulae, based on ordinary electrodynamics:

$$\chi(\nu) = \frac{\ln\left[\frac{I_0}{I}(1 - R')(1 - R'')\right]}{4\pi\nu d}, \tag{5}$$

where $\ln I_0/I$ is the recorded optical density of a crystal of thickness d; R' and R'' are the coefficients of reflection from the air-crystal interface, calculated by the Fresnel formula from the experimental dispersion curves.

The accuracy of the determination of χ depends on the errors in measuring the optical density and d. The optical density, taking account of reflection, was recorded in our experiments with an error of 5%. The thickness of the crystals was measured by a birefringence method (Berek compensator), and also by an interferometric method, with a mean error of 4%. Taking account of the finite thickness of the crystal and the resultant interference effect introduces a correction to $\chi(\nu)$ given by the formula (8):[1]

$$(6)\quad \Delta\chi(\nu) = \frac{1}{4\pi\nu d}\ln\left[1 - \frac{(1-\mu^2)(\mu^2-\mu_{кв.}^2)}{8\mu^2\mu_{кв.}}\cdot\frac{\cos 4\pi\nu\mu d}{\frac{I_0}{I}}\right].$$

Here μ_q is the index of refraction of the quartz plate. The correction $\Delta\chi$ calculated from equation (6) does not exceed 2 or 3% of the magnitude of χ for the thinnest crystals and decreases exponentially with thickness. Thus the mean error for a single measurement of χ equals 11-12%. And since the measurements were carried out on several crystals the error in the final dispersion curves does not exceed 6%.

The formula for computing the index of refraction is:

$$(7)\quad \mu(\nu) - 1 = \frac{\Delta I(\nu)}{H(\nu)\nu d},$$

where $\Delta I(\nu)$ is the displacement of the interference pattern due to the crystal and for a frequency ν, $H(\nu)$ is the width of the interference bands at the same frequency. The accuracy of a single measurement of μ in the absorption region is determined by the error in measuring the quantities which occur in equation (7) and is about 4% on the average. The variations of phase in the absorption region due to the complex refractive index and the finite thickness of the crystal do not exceed 2% in the worst cases. We used average dispersion curves, for which the error in a single value of μ is about 2-3%.

Let us briefly consider the crystallographic properties of the substances investigated. For anthracene, the crystallographic axes a and b lie in the well-developed plane faces of the monocrystalline slabs; moreover, the b axis coincides with the central axis N_m of the index-of-refraction ellipsoid, and the a axis subtends an angle of 30 degrees with the minor axis N_p. For crystals of 1, 2-benzanthracene the plane surfaces of the slabs coincide with the crystallographic plane (ab). However in this case not only does b coincide with N_m but also a coincides with N_p [9]. In the cases of stilbene and tolane, two axes of the ellipsoid, N_g and N_p, lie in the plane surfaces of the monocrystalline slabs. However it has been shown [10] that for stilbene the N_p axis coincides with the monoclinic axis. The optical characteristics of stilbene and tolane in the absorption region were determined from the very weak N_p-component of the absorption spectrum.

COMPARISON OF THEORY AND EXPERIMENT

A. 1, 2-Benzanthracene

The comparison is made for the b-components of the spectrum due to light polarized along the monoclinic axis of the crystal. The absorption and dispersion curves, measured in crystals with thickness $d = 0.35 - 0.40$ μ at 20°K., are shown in figures 1 and 2. As may be seen from fig. 2, the region of anomalous dispersion has not been measured throughout; however the measured values of μ do correspond to those expected from the half-width of the absorption bands. It follows that the measured values of μ go to the extreme, or are near to them (but do not exceed their outside limits). The experimental curve for $\chi\mu$ in the region from 25000 to 30000 cm^{-1} may be approximated by 15 Gaussian terms with an accuracy of 2% (of the area beneath the curve). The results of a calculation with equation (4), of that part of μ^2 which is due to the first two most important bands in the area of the spectrum investigated, are shown in Fig. 2. A calculation making use of additional short wavelength absorption bands would only result in decreasing the range in μ^2.

From this comparison of the calculated and measured values for the range of the μ^2 curves, it is apparent that the lack of agreement far exceeds the limits of the possible error in both the measurements and the calculations. Here and henceforth, as a measure of the disparity between theory and experiment, we will use the ratio of the range in the experimental curve for μ^2 to the range in the theoretical curve, taken in the region of the absorption band: $k = \Delta(\mu^2)_{exp.}/\Delta(\mu^2)_{theory}$.[2] It is necessary to emphasize that since $\Delta(\mu^2)_{exp.}$ cannot be overestimated (for the dispersion curve in relation to the usual theory), and since $\Delta(\mu^2)_{theory.}$ in the region of the long wavelength absorption bands will not be underestimated, then it is true that k is not overestimated (within the limits of error). For 1, 2-benzanthracene, $k = 4.4 \pm 0.9$.

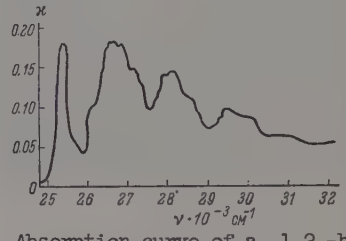


Figure 1. Absorption curve of a 1,2 -benzanthracene crystal at 20° K, ∥b

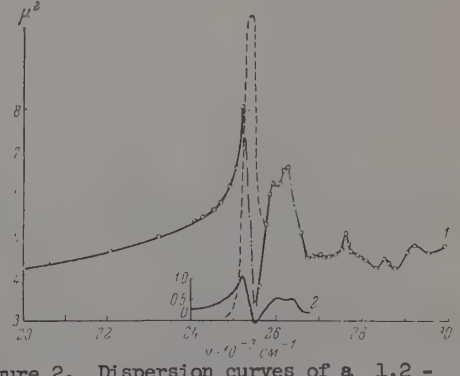


Figure 2. Dispersion curves of a 1,2 - benzanthracene crystal at 20° K, ∥b
1 - Experimental, 2 - Calculated

1. Reference is made to equation 4(71) in reference [8] for the amplitude of the transmitted light. We give here a formula derived from that one by changing to the intensity and by eliminating the coefficient of absorption in an obvious way.

2. Due to the errors in measuring and mentioned above, the error in the magnitude of k will be 20% in the worst case.

B. Anthracene

For the case of anthracene, the b-component of the spectrum was used also. Comparisons with formula (4) were made at temperatures of 20, 80 and 290°K. The original experimental data were taken from references [5] and [6]. Here, as for 1, 2-benzanthracene, due to the strong absorption at the maximum of the first band (see figures in the reference cited above) the region of anomalous dispersion could not be measured in its entirety, although in the present case the measured values of approach the extrema. The calculation was made for the important first long wavelength absorption band. At hydrogen temperature $k = 6 \pm 1$, and on raising the temperature to that of liquid nitrogen, k decreases to 3 ± 0.6, and finally at room temperature falls to 2 ± 0.4. Thus it is clear that in the case of anthracene, the divergence (between theory and experiment) is even greater than in the case of benzanthracene. Even at room temperature the divergence is considerable, in contrast to the examples cited in references [2] and [3] where there was agreement between theory and experiment at room temperature.

C. Stilbene (see reference [7])

The N_p-component of the spectrum was examined at the same three temperatures. It was found that at 20°K, $k = 4 \pm 0.8$, at 80°K, $k = 2.7 \pm 0.5$, and at room temperature the ranges in the two curves coincided (the comparison for 290°K was carried out in reference [7]).

D. Tolane

For the N_p-component of the tolane spectrum, as has already been mentioned, formula (4) is valid at room temperature [3]. From the work of reference [3] it was deduced that the N_p axis probably coincides with the monoclinic axis; hence it would be especially interesting to test the theory at low temperatures. Unfortunately, due to the lack of data on the dispersion in tolane crystals at 20°K, comparison was made only for nitrogen temperature. Here it turns out that $k = 2.2 \pm 0.4$; i.e. the divergence is already becoming considerable.

The results presented above demonstrate that in the case of several molecular crystals the general dispersion relations of Kramers and Kronig may be violated. Furthermore, this violation is greatest at low temperatures, and decreases as one goes to higher temperatures (on the average it decreases by a factor of three when the temperature is raised from 20 to 290°K). For several materials (stilbene and tolane) the Kramers-Kronig relations do hold at room temperature, within the limits of accuracy of the experiment. In the case of the sharpest breakdown (the b-component of anthracene), the experimental range in μ^2 is twice as great as the calculated one, even at room temperature. Hence it is concluded that in applications to the optical properties of crystals it is not possible to consider the Kramers-Kronig dispersion relations to be universally valid.

March 29, 1958

References

1. L. D. Landau, E. M. Lifshitz: Elektrodinamika sploshnym sred (Macroscopic electrodynamics), §62, Gostekhizdat, 1957
2. E. I. Rashba: Dissertation, Kiev, 1955
3. M. S. Brodin, A. F. Prikhot'ko: Ukr. Fiz. Zh., 3, 79 (1958)
4. K. A. Karpov: Tables of the function $w(z) = e^{-z^2} \int_0^z e^{x^2} dx$. Akad. Nauk SSSR Press, 1954
5. I. V. Obreimov, A. F. Prikhot'ko: Sbornik (Collection) in memory of S. I. Vavilov. Akad. Nauk SSSR Press, 1952
6. M. S. Brodin, A. F. Prikhot'ko: Opt. i Spektr., 2, 446 (1957)
7. M. S. Brodin: Dissertation, Kiev, 1956
8. O. S. Heavens: Optical properties of thin solid films. London, 1955
9. J. Iball: Z. Krist., 99, 230 (1938)
10. A. N. Winchel: Optical properties of organic compounds. New York, 1954

TOM VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar' , 1959
VOL. VI, No. 1 OPTICS AND SPECTROSCOPY January , 1959

AN OPTICAL INVESTIGATION OF THE MOLECULAR STRUCTURE OF s-TRIAZINE DERIVATIVES

IV.[1] Infra-Red Absorption Spectra Of Compounds With Condensed Nuclei Of s-Triazine-Derivatives Of Cyameluric Acid

A.I. FINKEL'SHTEIN

Abstract - Absorption spectra were obtained in the infra-red region (2-15 μ) of cyameluric acid and its derivatives: potassium hydromelonate, potassium cyamelurate, melem and deuteromelem.

It was established that in the IR spectra the cyameluric nucleus shows three characteristic absorption bands: two in the 6-7 μ region and one close to 12.5 μ. Examination of the absorption spectrum of melem has shown the correctness of the assignment by Redemann and Lucas of it as a derivative of cyameluric acid.

Derivatives of cyameluric acid are a highly interesting class of organic compounds. Discovered as long ago as the beginning of the last century [2-3] these compounds did not attract the attention of investigators for a long time. Only in 1937 did Pauling and Sturdivant subject the derivatives of cyanuric and cyameluric acids [4] to a comparative examination, and came to the conclusion that derivatives of cyameluric acid contain three condensed s-triazine nuclei. Cited here are the structural formulae of cyameluric acid [1], hydromelenic acid [2], melem [3] and others written down with the use of a system suggested by the author [5] of additional provisional designations (fig. 1).

The deductions of Pauling and Sturdivant concerning the structural formulae of derivatives of cyameluric acid were confirmed by a chemical investigation [6-7] and measurement of magnetic susceptibility [8].

However an investigation of the vibrational spectra of these compounds has not been carried out to the present time, although it can give a most straightforward confirmation to the attributed structural formula.

In the present work are cited the results of the investigation of the absorption spectra in the IR region of cyameluric acid and its derivatives: potassium cyamelurate, potassium hydromelonate, hydromelonic acid, melem and deuteromelem.

The absorption spectra were obtained for materials in the solid state compressed into translucent square pellets with powdered potassium bromide. Mixtures of powders were used with the concentration of the material investigated 1% in the 8-15 μ region, 0.33-0.1 % in the 2-8 μ region. The pressure for compression was equal to 10-12 t./cm^2 without use of vacuum. The square plates of 0.1-0.2 mm thickness which were obtained were mounted in front of the slit of the spectrophotometer by using a special holder.

For measurement of the spectra use was made of a single-beam infra-red spectrophotometer IKS-11 with a NaCl prism. Calculation of the spectra was carried out by the method of "null line", checked against the spectrum of a plate of pure KBr.

Potassium cyamelurate was prepared by hydrolysis of melone [6], cyameluric acid was obtained by acidifying a solution of potassium cyamelurate [6].

Potassium hydromelonate was prepared by melting melone with potassium thiocyanate followed by 8-10 recrystallizations from water in the presence of activated charcoal [6]. Hydromelonic acid was obtained by acidifying a solution of potassium hydromelonate.

Melem was obtained by heating melamine at 350°C for 30-40 minutes. Analysis of the quantity of ammonia arising in the decomposition of melamine, and determination of the unreacted melamine

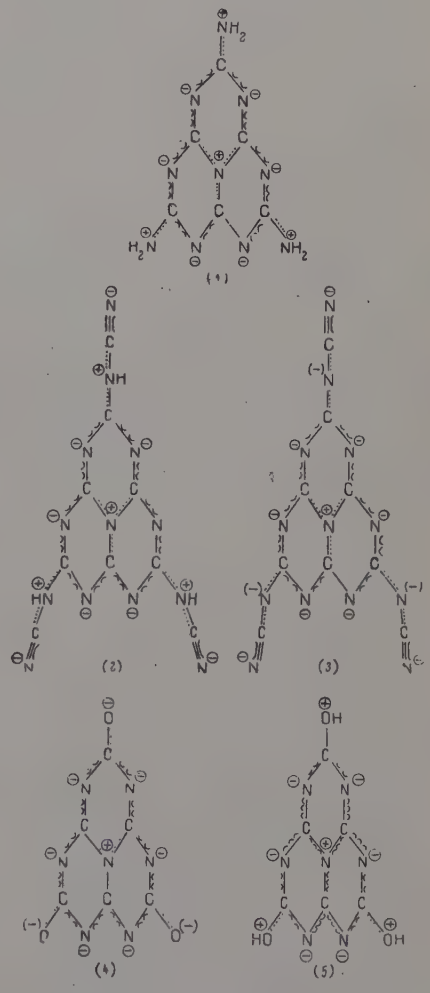


Fig. 1. The structural formulae of melem [1], hydromelonic acid [2], the hydromelonic acid anion [3], the anion of cyameluric acid [4] and cyameluric acid [5].

[1] For previous communication see ref. [1].

showed that the molar ratio of the quantity of reacted melamine and ammonia formed was equal to 1:1, which corresponds to melem. A detailed report of the synthesis of melem will be given elsewhere. Deuteromelem was obtained by heating deuteromelamine at 400° for one hour.

In the spectrum of potassium hydromelonate (fig. 2,A) attention is turned to the intense absorption band at 4.6-4.7μ, which can only be assigned to vibration of the triple bond C≡N.

The value of the frequency of the CN group in potassium hydromelonate at 2180 cm^{-1} is intermediate between the value of the CN frequency in cyanamide $H_2N-C\equiv\bar{N}$ at 2220 cm^{-1} and that of the sodium salt of cyanamide $Na^+(H\bar{N}-C\equiv\bar{N})$- at 2096 cm^{-1}. This phenomenon is explained by the fact that the negative charge with the nitrogen atom undergoes partial transition in the cyameluric nucleus, therefore the state of the cyanamid nitrogen in hydromelonate is much closer to the state of this atom in cyanamide.

In the 1400-1700 cm^{-1} region in the spectrum of potassium hydromelonate there are two bands: 1655 and 1430 cm^{-1}. The band at 1430 cm^{-1} is characteristic for the cyameluric nucleus just as the 1560 cm^{-1} band is characteristic for the s-triazine ring. The other band, at 1655 cm^{-1}, is, evidently, to a significant extent determined by the character of the external part of the molecule.

Characteristic for derivatives of cyameluric acid is the absorption band in the 12.5μ region (in the spectrum of potassium hydromelonate it is at 12.6μ). A band at a similar long wavelength is found in spectra of s-triazine derivatives.

In the spectrum of hydromelonic acid (fig. 2,B) are found three absorption bands in the 6-7μ region: 1695, 1615, and 1445 cm^{-1}. One of these (apparently the 1615 cm^{-1} band) is assigned to the deformation of the NH vibration. The value of the CN frequency here is 2245 cm^{-1}, which is close to the CN frequency in acetonitrile (2249 cm^{-1}) and slightly greater than in cyanamide. This is easy to explain by the fact that the nucleus of cyameluric acid is more electrophilic than the cyanide group, and draws to itself the unshared pair of electrons of the nitrogen atom.

The absorption spectrum of potassium cyamelurate (fig. 3,A) in large measure resembles the spectrum of potassium hydromelonate. The bands in the 6-7 micron region are shifted to longer wavelength and, accordingly, have $\nu_{max.}$ at 1500 and 1395 cm^{-1}. This may be connected with the significantly stronger transition, by comparison with potassium hydromelonate, of the negative charges to the cyameluric nucleus, which leads to greater stability of the ion and a greater degree of dissociation of cyameluric acid. Indeed, the first ionization constant of cyameluric acid is nearly to the fourth power greater than the first ionization constant of cyanuric acid. (1.0×10^{-3} and 1.66×10^{-7} respectively) [6].

The third characteristic frequency in the spectrum of potassium cyamelurate occurs at 12.35μ.

Cyameluric acid, in the same way as cyanuric acid, can give hydroxy and oxo forms. However, the absorption spectrum of cyameluric acid in the 6-7 micron region turned out to be exactly analogous to other derivatives containing the cyameluric nucleus. From this it follows that to extreme

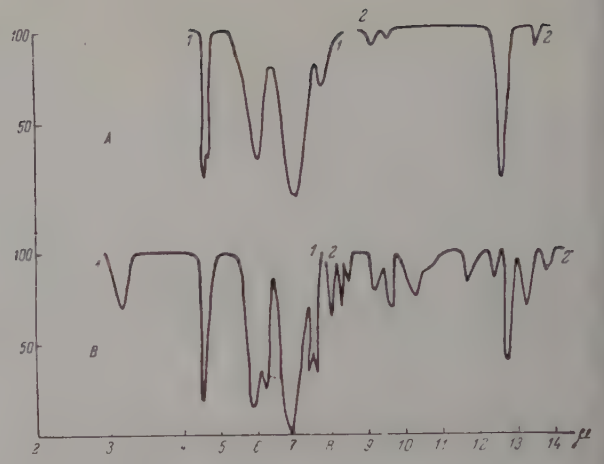


Fig. 2- IR spectra of potassium hydromelonate (A) and hydromelonic acid (B). 1-0.33%; 2-1%.

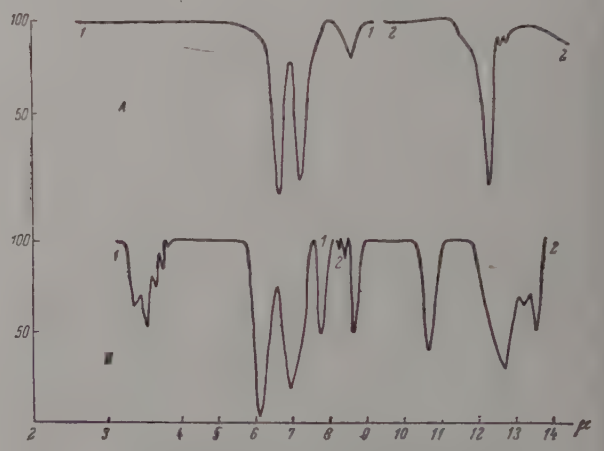


Fig. 3. The infrared spectra of potassium cyamelmate (A) and cyameluric Acid (B) 1 - 0.33%; 2 - 1%

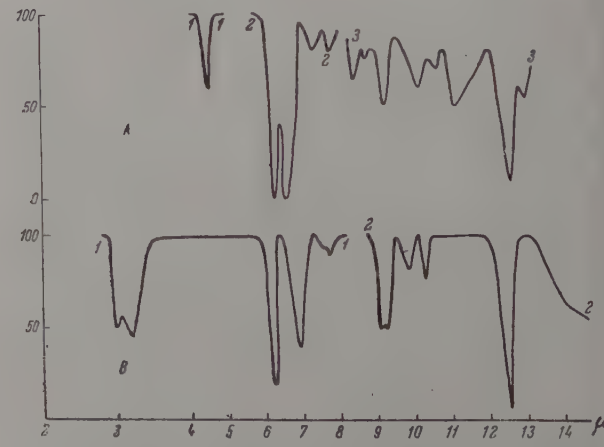


Fig. 4. The infrared spectra of deuteromelem (A) and melem (B)
1 - 0.33%; 2 - 1%; 3 - 3%

measure in the crystalline form cyameluric acid exists only in the hydroxy form.

In the region of OH stretching frequencies in the absorption spectrum of cyameluric acid (fig. 3,B) are found two intense and sufficiently wide bands (3.35 and 3.55 μ) and some less intense and longer wavelength bands (3.65, 3.75, and 3.83 μ). If the latter of these can be assigned to overtones, then the two former are evidence of the presence in cyameluric acid, just as in cyanuric acid, of two types of hydrogen bonds.

In the long wavelength region (8-15 microns) in the spectrum of cyameluric acid, except the characteristic band of the cyameluric nucleus with λ_{max} at 12.75, are found a group of bands which are assigned to the deformational vibrations of OH, and the stretching and deformation vibrations of CO.

The infrared spectrum of melem (fig. 4,A) offers considerable interest. Here all three bands characteristic for the cyameluric ring (at 6.20, 6.95, and 12.55 μ i.e. 1600, 1435 and 798 cm^{-1}) appear completely distinctly.

Since in the 6-7 micron region it is possible to find absorption bands corresponding to the NH deformation vibration, for evidence of the correctness of the assignment of the 6.20 and 6.95 micron bands in the spectrum of melem to vibration of the cyameluric ring we obtained the IR spectrum of deuteromelem (fig. 4,B). As is evident from fig. 4, in the spectrum of deuteromelem two absorption bands were indeed found in the 6-7 micron region, which are absent in the spectrum of the starting material, deuteromelamine.

At the same time, the band at 1560 cm^{-1} characteristic for derivatives of s-triazine was not found in the spectrum of melem. This result confirms the correctness of assignment of melem as a derivative of cyameluric acid, as was done by Redemann and Lucas [7], and contradicts the idea [8] that melem in its molecular structure has a s-triazine nucleus containing amino bridges.

Summing up the results obtained, we must note that the cyameluric nucleus is characterized by three bands in the infra-red absorption spectra: two in the 6-7 micron region, and one in the 12.5 micron region. Of these characteristic bands the one at longest wavelength is the most sensitive to the influence of substituents. The other two bands change to a lesser extent under the influence of substituents.

The characteristic bands indicated can be used for identification of the cyameluric nucleus in various compounds.

In conclusion the author expresses his gratitude to N.A. Gol'dberg for help in setting up and carrying out the work, and to A.K. Ermolaeva and L.S. Pugina for help in the work.

March 27, 1958

References

1. A. I. Finkel'shtein: Opt. and Spectr., 5, 264, (1958).
2. J. Liebig: Ann., 10, 10, (1834).
3. L. Gmelin: Ann., 15, 252, (1835).
4. L. Pauling, J. H. Sturdivant: Proc. Nat. Acad. Sci. 23, 615, (1937).
5. A. I. Finkel'shtein: Zh. Fiz. Khim. 31, 1659, (1957).
6. C. E. Redemann and H. J. Lucas: J. Am. Chem. Soc. 61, 3420, (1940).
7. C. E. Redemann and H. J. Lucas: J. Am. Chem. Soc. 62, 842, (1940).
8. J. Maruha: J. Chem. Soc. Japan, Pure Chem. Sect., 71, 627, (1950).

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

Infrared Absorption Spectra Of The Silicates Containing Aluminum And Of Certain Crystalline Aluminates.

V. A. KOLESOVA

Abstract - Infrared absorption spectra of the following thirteen crystals were investigated in the 410-1200 cm^{-1} region: corundum Al_2O_3, gallium oxide Ga_2O_3, hydrargillite $Al(OH)_3$, sodium aluminate $NaAlO_2$, albite $Na(AlSi_3O_8)$, orthoclase $K(AlSi_3O_8)$, feucite $K(AlSi_2O_6)$, nepheline $NaAlSiO_4$, cyanite Al_2O_6, α-spodumene $LiAl(Si_2O_6)$, β-spodumene $Li(AlSi_2O_6)$, jadeite $NaAlSi_2O_6$, and grossularite $Ca_3Al_2(SiO_4)_3$.

It is shown that in the spectra of aluminates and aluminum silicates in which the atoms of aluminum are in the anion shell, there is a band in the 720-780 cm^{-1} region, hypothetically attributed to the vibrations of the Al-O bonds.

At the present time, infrared absorption and reflection spectra of the majority of mineral crystalline silicates are known. The works of Matossi [1,2] and others [3-5] have shown that independent of composition and construction of the silicon-oxygen radical of the silicate, there always exists an intense and structually complex band in the 800-1100 cm^{-1} region of its infrared spectrum. This band is attributed to the vibrations of the Si-O bonds in the lattice of the silicate. It is further shown [2-4] that the position of this band in the spectrum is affected by the degree of polymerization of the SiO_4 tetrahedra in the lattice of the silicates: in the spectra of silicates with shell structure (a three-dimensional network of silicon-oxygen tetrahedra) the band occupies the highest frequency and in the spectra of orthosilicates (isolated SiO_4 tetrahedra) the lowest frequency position. The same dependence, of the absorption-maximum position in the band in this region of the spectrum on the degree of polymerization of the tetrahedra was observed in certain glass-type silicates both in the infrared and Raman spectra[7].

It is known, that in the lattice of the silicate the silicon atoms are always surrounded by tetrahedral groups of oxygen (coordination number equals 4). The distances Si-O are 1.60-1.62Å, and the forces bonding Si and O atoms are of covalent type.

A number of silicate minerals contain aluminum, the atoms of which, unlike the silicon atoms, may have varied coordination with respect to the oxygen atoms.

Indeed, on one hand it is known that in a large group of aluminum-containing silicates, for example in feldspars, aluminum atoms isomorphously replace silicon atoms forming a complex aluminum-silicon-oxygen shell, which consists of AlO_4 and SiO_4 tetrahedra. In this case coordination number of Al equals four, and the Al-O distances are 1.72-1.75Å. Al-O bonding forces, as in the case of Si-O, are of covalent type. In the future, speaking of Si-O covalent bond, also Al-O, let us always keep in mind the limitation of this definition, since the fraction of Si-O bond of covalent-character is no higher than 50%, according to Pauling. For the case of Al-O this fraction is lower yet.

On the other hand, in certain chain silicates and in orthosilicates the aluminum atoms do not enter the anion shell of the silicate and, in this case, replace alkali and alkaline-earth-metals and not the silicon atoms. Now the coordination number of aluminum atoms equals six and Al-O distances are 2.1Å. The bonding forces in this case are of ion type similar to O-Na or O-Ca bonds. Such a structure appears, in α-spodumene and jadeite (chain silicates) and in the group of aluminum garnets (orthosilicates).

The two types of Al-O bonds, considered above, should, undoubtedly, be displayed in different regions of the vibration spectrum of the mineral. When the atoms of Al enter into a common shell with atoms of Si and the Al-O bonds are of covalent type, it may be expected, that the frequency of vibration of this bond will lie in about the same region of the spectrum as the corresponding Si-O vibration. However, Al-O separation (1.72 Å) is considerably greater than Si-O separation (1.60 A). Besides, according to Pauling's electronegativity scale [9] , the degree of ionic character of the bond is greater in Al-O than in Si-O (see also [10]).

It is thus expected that the Al-O covalent-bond vibrations will correspond to lower frequencies than the frequencies of Si-O bonds.

The spectroscopic investigation of aluminum-containing silicates and in particular, determination of the frequency of Al-O bond vibrations in the spectra of a large number of objects may furnish valuable information about the structure of silicate's anion shell and the role played by aluminum atoms in its construction.

A very limited amount of information of spectroscopic display of Al-O bond has been published. E.g. in Refs.[1,3] the band in 690-735 cm^{-1} region in the infrared spectrum of such silicates as beryl and cyanite, is tied with AlO_6 octahedral vibrations. Also, while investigating the infrared absorption spectrum of aluminum soaps of various fatty acids the 990 cm^{-1} line was attributed to the Al-O covalent-bond vibration [11] .

We have obtained infrared absorption spectra of structurally varied silicates containing Al.

Besides, crystals not containing Si were investigated: corundum, hydrargillite and sodium aluminate (Table 1), and also crystalline gallium oxide which was obtained by roasting gallium nitrate at a temperature of 1300°C.

It is known, that physical and chemical properties of Al_2O_3 and Ga_2O_3 are quite similar and that these oxides may be considered as isomorphous compounds. Therefore, infrared spectrum of gallium oxide was investigated along with the spectrum of Al_2O_3.

Besides, we have obtained the spectrum of β-spodumene, which will be thoroughly discussed below.

Chemical analysis was conducted for all crystals except for jadeite and leucite, which were available in very small quantities and were analyzed spectrally only. In addition, indices of refraction were measured for all crystals.

TABLE I

COMPOSITION AND STRUCTURE OF INVESTIGATED CRYSTALS

NAME	FORMULA	ANION CONSTRUCTION	ORIGIN OF THE CRYSTAL
Corundum	Al_2O_3	AlO_6 octahedra	Synthetic
Hydrargillite	$Al(OH)_3$	Sheets of AlO_6 octahedra	Synthetic
Sodium aluminate	$NaAlO_2$	AlO_4 tetrahedra	Synthetic
Albite	$NaAlSi_3{}^-8$	Three-dimensional shell of SiO_4 and AlO_4 tetrahedra	Ural, Vishna mountains
Orthoclase	$KAlSi_3O_8$	Three-dimensional shell of SiO_4 and AlO_4 tetrahedra	Ural, Alobashka
Leucite	$KAlSi_2O_6$	Three-dimensional shell of SiO_4 and AlO_4 tetrahedra	Volcanic
Nepheline	$NaAl(AlSi_2O_8)$	Three-dimensional shell of SiO_4 and AlO_4 tetrahedra and a portion of Al atoms in AlO_6 octahedra (13)	Volcanic
Cyanite	Al_2SiO_5	SiO_4 tetrahedra bound to AlO_6 octahedra	Cola Peninsula
α - Spodumene	$LiAlSi_2O_6$	Chains of SiO_4 tetrahedra, Al - cation	China
Jadeite	$NaAlSi_2O_6$	Chains of SiO tetrahedra, Al - cation	Burma
Grossularite	$Ca_3Al_2(SiO_4)_3$	Isolated SiO_4 tetrahedra, Al - cation	Yakutia, Vilui River

The investigation was conducted in the 420-1330 cm^{-1} region using the vacuum spectrometer VIKSM-3 with NaCl prism and the spectrometer ISP-14b with KBr prism. The samples were prepared in the form of transparent discs, pressed from the mixture of the investigated substance and KBr. The concentration of the substance in the pressing process in all cases amounted to 15%. Besides, some samples were prepared in suspension form in paraffin oil. The spectra of the samples, prepared by the two described methods coincided; however, in all cases except Al_2O_3, the absorption peaks showed up clearer for the samples of the pressed type.

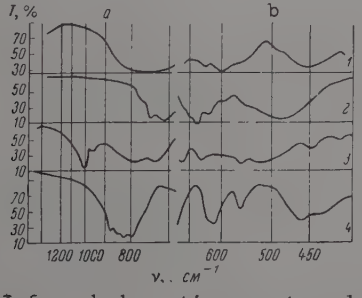


Fig. 1. Infrared absorption spectra. 1 - corundum AL_2O_3, 2 - gallium oxide Ga_2O_3, 3 - hydrargillite $Al^2(OH)_3$, 4 - sodium aluminate $NaAlO_2$. a - NaCL region, b - KBr region.

In Figures 1, 2, and 3 the left-hand side of the Figure is the NaCl region, right hand side the KBr region.

The absorption curves obtained are shown in Figs. 1-3. The frequencies of absorption maxima are given in table 2. Table 2 also contains the available data on the absorption spectra of the crystals. In the case of hydrargillite only, the data refers to its reflection spectrum [15], since its infrared absorption spectrum has not been published.

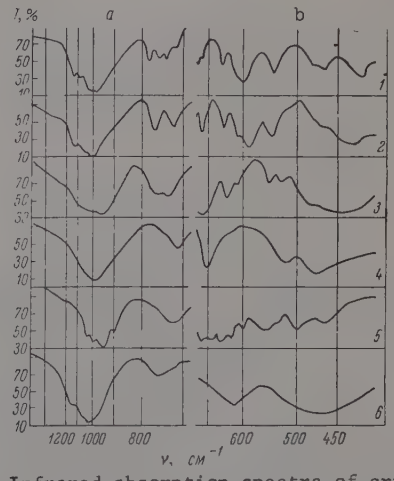


Fig. 2. Infrared absorption spectra of crystalline alumosilicates. 1 - albite $NaAlSi_3O_8$, 2 - Orthoclase $KAlSi_3O_8$, 3 - leucite $KALSi_2O_6$, 4 - nepheline $Na_2Al\ (AlSi_2O_8)$, 5 - Cyanite Al_2SiO_5, 6 - α spodumene $LiAlSi_2O_6$. a - NaCl region, b - KBr region.

TABLE 2

Location of Absorption Maxima in the Infrared Absorption Spectra of the Investigated Crystals (In cm^{-1})

corundum Al_2O_3		gallium oxide Ga_2O_3		hydrargillite $Al(OH)_3$		sodium aluminate $NaAlO_2$	albite $NaAlSi_3O_8$			orthoclase $KAlSi_3O_8$			leucite $KAlSi_2O_6$		nepheline $Na_2Al(AlSi_2O_8)$			cyanite Al_2SiO_5			β -spodumene $LiAlSi_2O_6$	α -spodumene $LiAlSi_2O_6$		jadeite $NaAlSi_2O_6$		grossularite $Ca_3Al_2(SiO)_3$
[17]	author	[17]	author	[15]	author	author	[4]	[18]	author	[3]	[15]	author	[5]	author	[4]	[5]	author	[3]	[5]	author	author	[3]	author	[3]	author	author
							1150	1160	1140										1162		1139		1132	1131		
										1130	1138	1132		1118								1116				
																			1106			1092				
							1099	1100	1098						1088	1084							1073	1070	1064	1061
								1040	1040	1036	1040	1044						1053			1049				
							1031	1020	1017				1030							1032		1031				
				1043	1020		1010														1017		1017			
												1007		1007	999	1000	983	1009		997				1002	995	
					967			990	987									972								
														951				946		940				935	926	940
																						927	917			
																		903	896	899	896					907
						874												882								
						847																864	862	860	858	
						827																				849
				796	791	804	789	790	787																	832
										776	771	769							800							
741	760		770			768	764	760	761					767	770				777		765					
		741	748	740	741		747	745	743															748	744	747
		700	722				725	730	719	728	724	723	724	735	736		745	734	727	730						
			[illegible]									709			713	714	711	684	711	710	698					
					670										690	700				684						
															667											
	642		646			638	650	650	652			649		629			637			656			642		663	635
						628			610			613		613						629						620
	602		602						598			590								598			596		590	
												552														
	559		542	549	562	562			536			540		549			536			552	560		542		532	543
				512	518	518						515		526			515			529						
	490		488						476			477								498			481		500–	485–
																									463	439
	450				452	464			464			465		479			474			464	470–				442	
																					430					
						443			432			439		446												

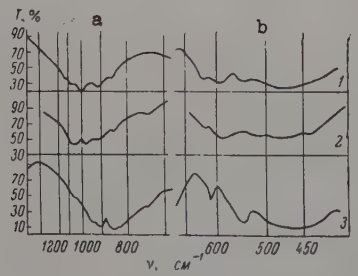


Fig. 3 Infrared absorption spectra of crystalline silicates of aluminum. 1 - α- spodumene $LiAlSi_2O_6$, 2 - jadeite $NaAlSi_2O_6$, 3 - grossularite $Ca_3Al_2(SiO_4)_3$. a - NaCl region, b - KBr - region.

The spectra of all crystals, containing silicon contained a wide band with a complex structure in the 1100-800 cm^{-1} region. The number of absorption peaks in this band and their intensity vary from one crystal to another. This band is due to the Si-O bond vibrations in the isolated SiO_4 tetrahedra or in the shelf of bound tetrahedra of various silicates. The center of this band is being shifted somewhat toward lower frequencies as we go from the silicates with a three-dimensional shell (albite, leucite and others) to chain silicates (α -spodumene, jadeite) or to the orthosilicate - grossularite.

The biggest shift occurs in the spectrum of grossularite and its lowest-frequency peak is at 747 cm^{-1}.

Naturally, this band is absent in the spectra of crystals, which do not contain silicon. The 1020 and 967 cm^{-1} lines, observed in the spectra of $Al(OH)_3$ correspond, it seems, to the elastic vibrations δ(OH) of the hydroxyl groups.

A strong absorption is observed in the 720-780 cm^{-1} region of the crystalline-aluminates spectra. In the same 720-780 cm^{-1} region a band was observed also in the spectra of aluminum silicates, where Al isomorphously replaces Si, i.e. where Al is in the anion shell of the crystal and where Al-O bond is of covalent character. This band is complex, in many cases it consists of several components and only in the case of corundum Al_2O_3 has a shape of a broad simple maximum.

In the spectra of crystals, in which atoms of Al are not in the anion shell but serve as cations, i.e. are far 2.1 Å from the oxygen atoms and are bound to them with ionic forces, we do not observe the band in the 720-780 cm^{-1} region.

We have investigated the spectra of three such crystals: α -spodumene, jadeite and grossularite. The spectra of these crystals show that the band in the 720-780 cm^{-1} region is absent, as seen in Fig. 3.

These facts led us to the assumption that the band in the 720-780 cm^{-1} region is caused by the valence oscillation in the aluminate's anion shell just as the band in the 800-1100 cm^{-1} region is caused by the valence oscillation of Si-O in the silicate's lattice.

The comparison of corundum Al_2O_3 and gallium oxide Ga_2O_3 spectra (Fig. 1a) has shown, that the intense band observed in the Al_2O_3 spectrum, has been shifted toward lower frequencies in the gallium oxide spectrum. It seems, that it was caused by the replacement of Al atoms by the heavier Ga atoms. This band shift confirms its reference to the Al-O vibration in case of corundum and to the Ga-O vibration in case of gallium oxide.

We have conducted an experiment on spodumene in order to confirm the accuracy of referring the 720-780 cm^{-1} band to the "short" Al-O covalent-bond vibration. It is known that natural spodumene, characterized by chain radical which is made up of SiO_4 tetrahedra, has a second β modification, whose lattice is similar to the lattice of feldspars. In the β -spodumene lattice Al atoms isomorphously replace Si atoms, forming a three dimensional shell made up of AlO_4 and SiO_4 tetrahedra. Therefore, it was especially interesting to conduct an investigation of the vibration spectra of both α - and β - spodumene.

If the presence of Al atoms in the anion shell of the crystal is the cause of the band observed in the 720-780 cm^{-1} region of its infrared spectrum, then it is expected that the band will appear in the β - and not in α - spodumene spectrum.

We derived β - spodumene by heating natural α- spodumene in a platinum crucible at a temperature of 1000°C for 3 hours, followed by slow cooling. The fullness of α→β conversion was determined from the index of refraction of the product. X-ray scattering curves were obtained for both forms of spodumene, which clearly indicated the differences in their lattice structures.

Let us now look at the obtained infrared spectra of α - and β - modifications of spodumene. As seen from Figs. 2a and 3a they are sharply different from each other. First of all, the band of Si-O vibrations of the β - spodumene spectrum lies in the region of higher frequencies than the one of α - spodumene due to higher degree of polymerization. of anion shell from chain in α - to three-dimensional in β -. Further, in the 760 cm^{-1} region, while the α - spodumene spectrum has no absorption band, β - spodumene spectrum contains an intense well pronounced band, located at the same frequencies as in the spectra of feldspars and other crystals - whose anion shells contain Al.

Thus, the spodumene experiment confirmed our thought that the presence or absence of 720-780 cm^{-1} band in the infrared absorption spectrum determines the role played by Al atoms in the lattice of the aluminum-containing crystals: i.e. 720-780 cm^{-1} band is observed in the spectra of those crystals, whose lattice contains Al atoms as participants of the anion shell construction.

It is interesting to note that the band of vibration of Al-O covalent bond, always appears in the same 720-780 cm^{-1} region, independent of the coordination number of Al atoms with respect to oxygen atoms.

Thus, for instance, in the spectra of Al_2O_3 and $Al(OH)_3$ where Al is in AlO_6 octahedra as well as in spectra of feldspars where Al is surrounded by O atoms forming AlO_4 tetrahedra, the band has practically the same frequency. It may be assumed, that the frequency of this band is determined by the character of Al-O bond, by the fraction of its covalency. An increase in the ionic character of the bond, i.e. transfer of Al atoms from anion shell into cation state, eliminates the 720-780 cm^{-1} band from the spectrum. It is expected that Al-O ionic-bond vibration must lie in the low frequency region. However the spectra of the majority of the crystals, containing aluminum, investigated by us, are so complex in the 410-660 cm^{-1} region, that a definite identification of that band is not yet possible.

Let us note further, that the position of the discussed band in the spectrum does not depend on which atom is oxygen atom bound to, in the system Al-O-X.

Indeed, in cases of Al-O-Al (corundum), Al-O-H (hydrargillite) and finally Al-O-Si (feldspars and other aluminum silicates) the band is always located in the same 720-780 cm^{-1} region. (Fig. 1, 2). In the case of sodium aluminate, however, (bonds Al-O-Na) the band is shifted somewhat toward higher frequencies and its center is located at 850 cm^{-1}. It should be noted, that according to [12] , the Al-O distance in potassium and sodium aluminates is considerably smaller than in feldspars and amounts to 1.66 Å. It seems, that an increase in frequency of Al-O vibration in the spectra of those compounds is due to the distance consideration.

The fact that cyanite spectrum also contains the 720 cm^{-1} band allows us to draw certain conclusions about its structure. Usually cyanite is referred to the orthosilicates group, since the SiO_4 tetrahedra in its lattice are not immediately bound to each other, but through AlO_6 octahedra. However, our data allows us to assume, that at least a portion of Al atoms is bound to oxygen atoms in the cyanite lattice by covalent forces and participates in the formation of anion shell of that crystal.

The author is very grateful to N.V. Belov for interesting and valuable discussions on the results of the work, as well as to E.F. Gross on his interest in the work and consideration of the results.

February 28, 1958

References

1. C. Shaefer, F. Matossi, K. Wirtz: Z. Phys., 89, 210 (1934).
2. F. Matossi, H. Krueger: Z. Phys., 99, 1 (1936).
3. P. Launer: Am. Mineral., 37, 764 (1952).
4. J. Hunt, M. Wishard, J. Bonham: Anal. Chem., 22, 1478 (1950).
5. W. Keller, J. Spotts, D. Biggs: Am. J. Sci., 250, 453 (1952).
6. V. A. Florinskaia, R. S. Pechenkina: DAN USSR, 89, 37 (1953); 91, 59 (1953).
7. E. F. Gross, V. A. Kolesova: Sb. "Stroenie stekla" (Structure of glass). Moscow-Leningrad, 1955.

References (continued)

8. V. S. Sobolev: Vvedenie v mineralogiiu silikatov (Introduction to the mineralogy of silicates) L' vov, 1949.
9. L. Pauling: Nature of the Chemical Bond. 2d. ed. Ithaca, Cornell Univ. Press, 1940 (Russian translation, 1947)
10. A. S. Povarennykh: DAN USSR, 109, 993 (1956).
11. W. W. Harple, S. E. Wiberley, W. H. Bauer: Anal. Chem., 24, 635 (1952).
F. A. Scott, J. Goldenson, S. E. Wiberley, W. H. Bauer: J. Phys. Chem., 58, 61 (1954).
12. T. F. Barth: J. Chem. Phys., 3, 323 (1935).
13. N. V. Belov: Tr. Inst. Kristallogr., 10 (1954).
14. L. M. Foster, H. C. Stumpf: J. Am. Chem. Soc., 73, 1590 (1951).
J. Kohn, G. Katz, J. Broder: Amer. Mineral., 42, 398 (1957).
15. F. Matossi, H. Bluschke: Z. Phys., 108, 295 (1938).
16. O. Glemzer, E. Hartert: Naturwiss., 40, 552 (1953).
17. E. G. Brame, Jr., J. L. Margrave. V. W. Meloche: J. Inorg. Nucl. Chem., 5, 48 (1957-58).
18. F. Laves, St. Hafner: Z. Kristall., 108, 52 (1956-57).

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

Absorption Spectra And Raman Spectra Of Selenophene And Its Methyl Homologues

N. A. CHUMAEVSKII, V. M. TATEVSKII, AND IU. K. IUREV

Abstract - Absorption spectra in the ultraviolet and infrared regions, and Raman spectra of selenophene, 2- and 3- methylselenophene, 2, 3-, 2, 4-, and 3, 4-dimethylselenophene have been studied. The characteristic frequencies of the selenophene ring, substituted at various positions, have been established.

In the present work, the absorption spectra in the infrared and ultraviolet regions, as well as the Raman spectra for selenophene, 2- and 3-methylselenophene, and 2,3-, 2,4-, 3,4-dimethylselenophene have been investigated.

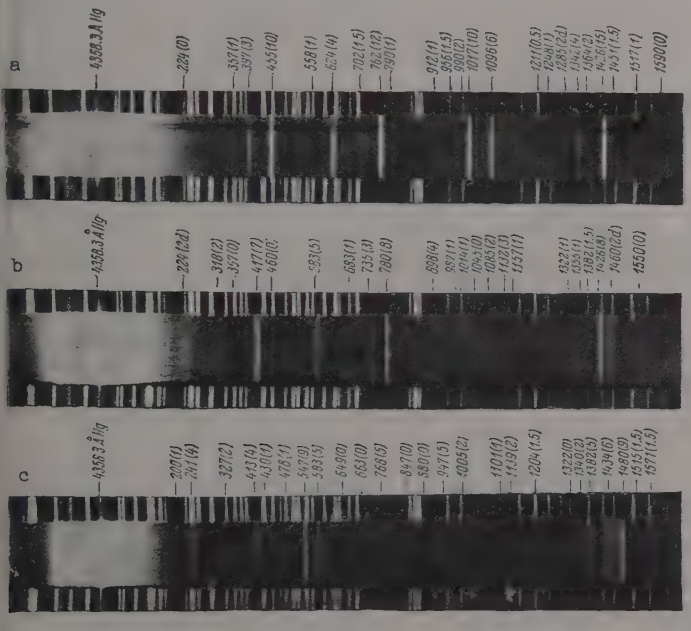


Fig. 1
Raman Spectra

a - selenophene, b - 3- methylselenophene, c - 2,4-dimethylselenophene (ω_i wave number)

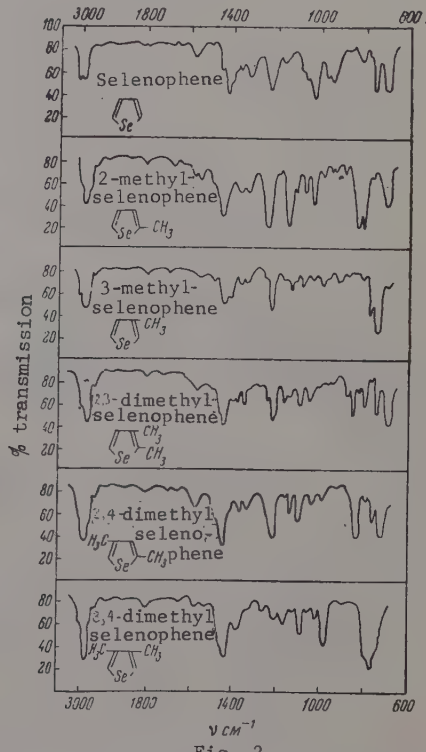


Fig. 2
Infrared absorption spectra of selenophene and its methyl homologues (NaCl prism, double beam).

Spectroscopic data concerning these substances (with the exception of selenophene itself [1]) are not available in the literature. On derivatives of selenophene there has been only one piece of work [2] in which an investigation was made of the infrared absorption spectra of alkoxy- and vinylselenophenes and also of certain other selenophene derivatives substituted at the 2,4- positions.

In all substances that we investigated, we observed a definite number of more or less intense frequencies which occurred both in the infrared absorption spectra and in the Raman spectra, and which are characteristic of this group of compounds. (See Fig. 1 & 2)

In the region of valence vibrations of ring CH groups absorption bands were found in the infrared spectrum of selenophene at 2960 and 3050 cm^{-1}; for the methyl homologues of selenophene, bands were observed at somewhat smaller wave numbers, namely, in the 2950 cm^{-1} region. For homologues of selenophene an absorption band characteristically occurs in the region of 2750 cm^{-1}. The intensity of this band increases with an increase in the number of CH_3 groups, as is easily evident in a thick layer (50 μ) of substance.

The vibration frequency of the C=C double bond in a selenophene ring has a value of 1582 cm^{-1} (infrared absorption spectra); it is rather small in intensity, and in the homologues it is somewhat displaced in the direction of smaller wave numbers; where for 2-methylselenophene and 3,4-dimethylselenophene the infrared absorption spectra in this region posses the two frequencies: 1550, 1575 and 1540, 1575 cm^{-1}, respectively.

It is necessary to mention that the frequencies, corresponding to the vibration of the C=C double bond in thiophene and its homologues are found in the infrared absorption spectra in the region 1580 cm^{-1} [3,4] . Absorption in this region is also characteristic for certain aromatic compounds pyridine [5] and octatetraene [6] .

Fundamental vibration frequencies of the heterocycle (1032-1019, 1079-1086, 1358-1349, 1404-1428 cm^{-1}), practically coincide in thiophene

*Ed. Note-The reference referred to deals with cyclooctatetraene. Neither is generally considered to possess aromatic properties. - J.S.W.

Vibration frequency of Selenophenes

Selenophene		2-methylselenophene		3-methylselenophene		2,3-dimethylselenophene		2,4-dimethylselenophene		3,4 dimethylselenophene	
Raman spectrum	Infrared absorption spectrum	Raman spectrum	Infrared absorption spectrum	Raman spectrum	Infrared absorption spectrum	Raman spectrum	Infrared absorption spectrum	Raman spectrum	Infrared absorption spectrum	Raman spectrum	Infrared absorption spectrum
						200 (0)?		200 (1)		210 (1α)	
224 (0)		228 (1.5)		224 (2α)		241 (1)		241 (4)		257 (0)	
357 (1)		266 (2)		318 (2)		325 (2)		327 (2)			
397 (3)	400 C	421 (1)	—	357 (0)		406 (5)	415 И	413 (4)	420 И	402 (6)	405 И
455 (10)	460 И	440 (2)	437 И	417 (7)	413 И	434 (1)	—	430 (1)	—	428 (2)	—
—	—	—	540 C	460 (0)	456 C	546 (1)	552 C	478 (1)	—		
558 (1)	550 C	563 (6)	570 C	—	473 C	565 (5)	570 И	547 (9)	552 И	541 (4)	540 C
—	590 C	595 (0)	595 M	—	540 M	637 (7)	640 И	583 (5)	589 И	582 (0)	590 C
624 (4)	630 C	652 (7)	660 И	583 (5)	590 И	—	690 И	649 (0)	645 M	644 (0)	645 M
702 (1.5)	702 И	—	700 C	—	635 M	745 (5)	750 И	663 (0)?	660 O. M.	683 (0)	680 M
762 (12)	763 И		803 } И	683 (1)	675 M	—	800 C	—	720 И		
790 (1)	805 M	800 (1.5)	830 }	735 (3)	743 И	—	830 M	768 (5)	770 И	745 (9)	752 } И
—	860 O. M.	894 (0)	890 M	780 (8)	780 И	853 (1)	850 И	—	790 M		784 }
912 (1)	—	—	935 M	—	800 M	870 (0)	875 M	—	840 И	792 (3)	
956 (1.5)	950 C	975 (1)	976 M	898 (4)	903 C	929 (0)	940 O. M.	847 (0)	—		
990 (2)	—			987 (1)	—	—	960 O. M.	880 (0)	—	912 (0)	910 O. M.
1017 (10)	1027 И	1036 (1)	1035 C	1014 (1)	995 C	1056 (1)	1050 C	947 (5)	940 O. M.	—	985 И
1096 (6)	1087 C	—	1070 C	1045 (0)	1040 M	1107 (1)	1098 И	1005 (2)	997 M	1009 (1)	1020 M
—	1170 M	1095 (3)	—	1085 (2)	1080 C	1144 (1)	1150 M	—	1035 M	1085 (1)	1082 C
1211 (0.5)	—	1144 (1)	1147 И	1132 (3)	1130 C	—	1175 C	1101 (1)	1102 C	1145 (3)	1120 M
1248 (1)	1243 И	1245 (2)	1240 И	1157 (1)	1150 O. M.	—	1220 И	1139 (2)	1135 C	—	1175 C
1285 (2d)	—	1270 (0)	—	—	1220 И	1250 (0)	1260 O. M.	1204 (1.5)	1209 И		1220 C
1342 (4)	1333 C	1332 (3)	1330 C	1322 (1)	—	1347 (1)	1345 C	1322 (0)	—	1235 (0)	1240 M
1364 (2)	1370 M	1378 (1.5)	1372 C	1355 (1)	1350 M	1382 (2)	1375 C	1340 (2)	1340 C	1359 (3)	1370 C
1426 (15)	1422 И	1397 (1)	—	1382 (1.5)	1375 M	1453 (12)	1448 И	1382 (5)	1375 C	1428 (5)	1435 И
1451 (1.5)	1448 C	1459 (10)	1450 И	1426 (8)	1432 И	1502 (1.5)	—	1434 (6)	1440 И	1493 (3)	—
1517 (1)	1510 O. M.	1550 (1)	1550 C	1460 (2α)	—	1520 (1.5)	—	1480 (9)	—	—	1540 M
1590 (1)	1582 M	—	1575 C	—	1485 M	1571 (0)	1565 M	1515 (1.5)	—	1570 (0)	1575 M
				1550 (0)	1550 M			1571 (1.5)	1570 C		
	2960 } И		2950 И		2950 И		2930 И		2950 И		2940 И
	3060 }		—		—		—		—		—
Overtones and combination frequencies (in a thick film) (50μ)	1840 И		1850 И		1795 И		1800 И		1852 O. M.		1800 M
	2040 M		2040 M		1900 M		—		1910 M		1880 M
	3900 И		3850 И		3900 C		3910 C		3900 M		3900 И
	4400 M		4400 И		4400 И		4400 И		4400 И		4400 И
	5800 C		5800 M		5800 C		5800 M		5800 M		5800 C

И - intense band, C - medium intensity, M - small intensity, O.M. - very small intensity

and selenophene. Our frequency values for selenophene-1017, 1096, 1342 and 1426 cm^{-1} in the Raman spectrum and the corresponding values (see table) in the infrared spectrum are in a good agreement with the above mentioned values.

The vibration frequency of 1422-1426 cm^{-1} remains unchanged in the case of 3-methylselenophene and 3,4-dimethylselenophene; for the other methyl homologues the vibration frequency is somewhat larger (1450cm^{-1}); in the Raman spectrum of 2,4-dimethylselenophene the characteristic frequencies 1434 and 1480 cm^{-1} occur, and in 3,4-dimethylselenophene they are 1428 and 1493cm^{-1}.

The C--Se bond vibration frequency appears to lie in the 700-800cm^{-1} region; for selenophene the characteristic frequencies in this region are 702 and 762cm^{-1}. In the spectra of the homologues, the frequencies observed have different values (see table). In the literature [1,2] the vibration frequency of the C--Se bond is reported as 762cm^{-1}. The frequency 832cm^{-1} [4] corresponds to vibrations of the C-S bonds in thiophene.

In all substances that we investigated in the infrared (excluding 3,4-dimethylselenophene) we observed characteristic intense absorption bands in the region 1209-1250 cm^{-1} which were also observed in homologues of selenophene with the 2,4-position substituted. Coincidence of frequencies (3075-3050, 1250, 1426 cm^{-1} and others), and the common resemblance of the infrared absorption spectra of thiophene, selenophene and their homologues, serves as confirmation of the planar structure of selenophene; one may assume that selenophene belongs to the symmetry group C_{2v}.

The results obtained by us on the Raman spectra and on the infrared absorption spectra for selenophene itself are in good agreement with the data available in the literature [1].

In general the spectra of selenophene and its homologues display characteristic frequencies that depend upon the vibrations of the substituents. (See Table)

The ultraviolet absorption spectra which we took of selenophene and its methyl homologues, (in the region 2200-2800Å) did not show any essential difference in the electronic transition at 2500Å. (Fig. 3). It therefore follows that analogous spectra for thiophene and its methylhomologues will not manifest any differences.

EXPERIMENTAL PART

Raman spectra were taken with a Steinheil spectrograph (f 640mm, linear dispersion o.1mm/Å) with a vertical light source of Sharigin type construction.

The absorption spectra in the infrared region were taken with a single-beam infrared spectrometer type IKS -11, with three prisms: LiF (3300-6000cm^{-1}) NaCl (660-3000cm^{-1}) and KBr (400-600cm^{-1}), and with a wedge of constant thickness (50 μ) and KBr windows. Some of the spectra were taken with an infrared, VIKSM-3 spectrometer, having a NaCl double beam prism.

The ultraviolet absorption spectra for selenophene and its methyl homologues were taken in isooctane with an SF-4 [1] spectrophotometer.

Selenophene and its homologues studied in the present work had the following constants (after distillation through a tall column and then through a fractionating column of 18 theor. plates).

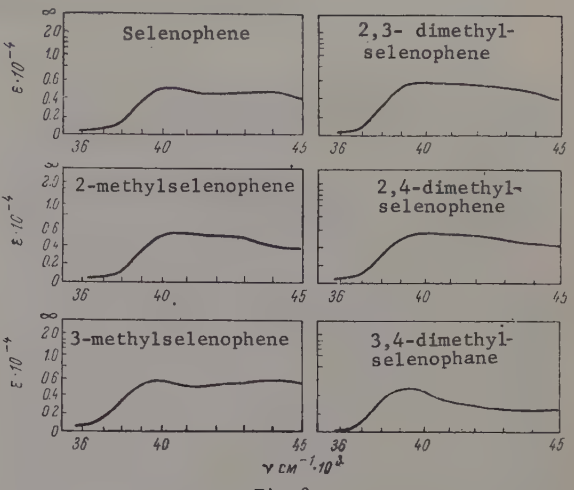


Fig 3

Ultraviolet absorption spectra of Selenophene and its Methylhomologues (in isooctane)

The Raman spectra and the infrared absorption spectra obtained from selenophene and its homologues can be utilized for their identification.

Selenophene: b.p. 110.5-111 (753mm), n_D^{20} 1.5715; d_4^{20} 1.5358; MR_{D2} 28.05 . C_4H_4Se F_2. Calculated[4] MR_D 28.17.

2-Methylselenophene: [8] b.p. 136-136.2 (769 mm); n^{20} 1.5615; d_4^{20} 1.4432; MR_D 32.57. C_5H_6Se F_2. Calculated; MR_D 32.79;

3-Methylselenophene: [9] b.p. 137-137.5 (751mm); n^{20} 1.5615; d_4^{20} 1.4623; MR_D 32.15. C_5H_6Se F_2. Calculated; MR_D 32.79.

2,3-dimethylselenophene [10] : b.p. 159.5-160 (756 mm); n^{20} 1.5539: d_4^{20} 1.3734; MR_D 37.16. C_6H_8Se F_2. Calculated; MR_D 37.38.

2,4-dimethylselenophene [10] : b.p. 159.5-160 (746mm); n_D^{20} 1.5498; d_4^{20} 1.3672; MR_D 37.07. C_6H_8Se F_2. Calculated: MR_D 37.38.

3,4-dimethylselenophene [9] ; b.p. 168-168.5 (743mm); n_D^{20} 1.5565; d_4^{20} 1.3945; MR_D 36.66. C_6H_8Se F_2. Calculated: MR_D 37.38.

March 31, 1958

NOTE

1 Infrared absorption experiments spectra using the VIKSM-3, and ultraviolet absorption spectra using the SF-4 spectrophotometer were performed in the I.N.E.O.S. Optical laboratory of the USSR Academy of Science.

2 Atomic refraction for -Se- in selenophene and its methylhomologues is assumed to be equal to 10.61 [11] .

References

1. H. Gerding, G. Milazzo and H. Rossmark: Rec. trav. chim. 72, 957 (1953)
2. F. Ia. Perveev, and D.N. Glebovskii, Bull. LGU, No. 22, 135 (1956)
3. A. Hidalgo. C.R., 239, 253-255 (1954)
4. A. Hidalgo: J. Phys. Radium, 16, No. 5, 366, (1955)
5. L. Bellamy "Infrared Spectra of Molecules" p. 82, (1957)
6. E. Lippincott, J. Am. Chem. Soc., 73, 3370 (1951)
7. H. Hartough. "Thiophene and its Derivatives". Interscience Publishers, Inc., N.Y., 102 (1952)
8. Iu. K. Iurev, N.N. Mezentsova and V.E. Vaskovskii, (Zh. Org. Ch.), 27, 3155 (1957)
9. Iu. K. Iurev and L. I. Khmelnitzkii Doklady Akad Nauk. USSR, 94, 265, (1954)
10. Iu. K. Iurev, N.K.Sadovaia and M.A.Gal bershtam, Zh. Org. Kh. 28, 627, (1958)
11. B. Tamamushi, H. Akiyama and S. Umezawa, Bull. Chem. Soc. Japan., 14, 310, (1939)

TOM VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar' , 1959
VOL. VI, No. 1 OPTICS AND SPECTROSCOPY January , 1959

Influence of the Refractive Index of a Dispersing Medium on the Raman Spectrum Line Intensity

A. I. SOKOLOVSKAIA, S. G. RAUTIAN

Within recent years, a number of works has appeared in which the necessity is indicated of taking into account the refractive index of the dispersing substance n_f in measurements of the Raman spectrum line intensity [1-3].* Such a calculation is necessary in investigations of the temperature dependence of the line intensity, in the comparison of the line intensities of pure substances and solutions and also in the variation of the frequency of the exciting radiation. Let us briefly enumerate the reasons for which the line intensity can depend on n_f.

The flux incident on the external surface of the sample is determined just by the source and the condenser system and is independent of the refractive index of the fluid n_f. The magnitude of the flux entering the sample depends on the ratio of the refractive indices of the fluid n_f and the container wall n_w[2] because of the reflection on the glass container-fluid interface. On leaving the fluid, the exciting radiation is partially reflected within the container, which leads to a decrease in the influence of the former reflection [4,7].

The dispersing sample exerts a certain focussing effect on the beam of exciting radiation. Since this effect is determined by the fluid refractive index, then (depending on its magnitude) some kind of ray configuration of the exciting radiation will exist within the vessel, which is an additional cause of the influence of n_f on the magnitude of the Raman bond intensity being measured.

On leaving the container, the intensity of the scattered light diminishes by n_f^2/n_{air} [1,8].** Moreover, depending on the quantity n_f, the reflection conditions of the dispersing volume by the slit of the spectrograph change, which can also distort the magnitude of the line intensities being observed [3].

Hence, the whole set of effects related to the variations of the fluid refractive index reduce to the following: 1) a change in the reflection coefficient on the fluid-glass container interface; 2) a change in the ray configuration of the exciting light within the container; 3) a change in the intensity of the scattered radiation on leaving the container; 4) a change in the reflection conditions of the container by the slit of the spectrograph.

It is essential to note that only the third factor is subject to a rigorous theoretical computation. The effect of the rest can change radically from one apparatus to another and to take them into account by computational means is impossible in practice. Such a situation lead the authors of [2,3] to the conclusion that the single possibility of avoiding systematic errors consists of calibrating the apparatus according to sample etalons. For example, the refractive index of the dispersing fluid can be changed by changing its temperature or the solution concentration and to calibrate the line intensity according to a known concentration (or temperature) dependence. But precisely to explain such a dependence it is also necessary to know the influence of the refractive index of the sample and there are no reliable measurements, at the present time, in which these apparatus errors would be taken completely into account. Therefore, the recommendation of [2,3] leads to a closed circle. The escape from the situation thus created can be, say, that an experimental study of the part of n_f would be made on the same dispersing substance, i.e., without changing n_f itself. One of the possible variations of such a solution of the problem is described herein.

The following method was used to measure the reflected share of the exciting radiation. A container with the dispersing fluid was placed in a glass tube (see fig.1); fluids with different refractive indices were poured in turn into the space formed. The two glass-fluid and fluid-glass interfaces simulate a single boundary, which occurs in the ordinary measurements, and they double the refractive index approximately. It is essential that the dispersing fluid remain the same but a change in the path of the rays within the container need not be feared for thin enough walls and gap and just a change in the reflection of the incident rays can be investigated.

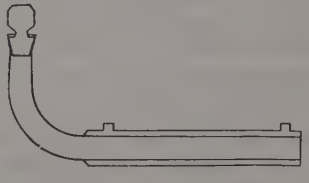


Figure 1. Diagram of a container with double walls.

The thickness of the wall of the additional tube in the container we used was 0.7 and the gap was 0.5 mm. Benzene and toluene were used as dispersing fluids. The gap was filled in sequence by carbon bisulfide (n = 1.67), benzene (n = 1.52), toluene (n = 1.52), and ethyl alcohol (n = 1.36). Experiments were also conducted without filling the gap (n = 1). The refractive index of the container wall was $n_w = 1.52$. All the measurements were made by a photographic method. The spectra of the dispersing substance and of the mercury lamp were recorded simultaneously on the photographic film, which permitted elimination of fluctuations in the intensity of the exciting radiation.

The results of the measurements are given in figure 2. The ratio of the refractive indices of the fluid in the gap n_f' and the container wall n_w is plotted along the horizontal axis and the change in the flux of the exciting light, calculated according to the ratio of the Raman spectrum line intensity for various fluids in the gap, along the vertical. Each point on the graph is the result of averaging approximately 60 measurements. The root mean-square error in the measurements does not exceed 1%.

As is seen from figure 2, the incident flux changes by 6% as n_f' varies between 1 and 1.52 but this change will be about 3% in the presence of one interface. For real fluids n_f lies within the range

* A similar situation holds also in a number of cases, in particular, in the measurement of the Rayleigh light scattering intensity (see [4-6], for example). However, there exist specific pecularities in the apparatus, which oblige these cases to be considered separately.

** The intensity certainly diminishes also because of reflection on the fluid-glass and glass-air interfaces. However, the reflection coefficient in the first case does not exceed tenths of a percent and in the second is the same for all fluids.

from 1.3 to 1.7 and the possible correction ($\sim 1\%$) for the container usually used is much less than the error in the photographic photometry.

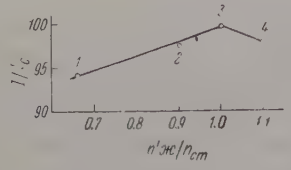


Figure 2. Dependence of the exciting light flux on the refractive index n_f' of the substance in the gap. 1 - $n_f' = 1$ (air); 2 - $n_f' = 1.36$ (alcohol); 3 - $n_f' = 1.52$ (benzene, toluene); 4 - $n_f' = 1.67$ (carbon bisulfide); $I_0 = 100$ is the line intensity in a gap filled with benzene or tolene. (n_f'/n_w)

Now, let us turn to an analysis of the fourth factor, namely, the influence of the conditions of mapping the vessel by the slit of the spectrograph. If the sample is irradiated uniformly, then the condensing system can be selected so that the image of the slit and the mounting of the collimator lens would be less than the irradiated part of the container for all values of n_f.* In this case, the irradiation of the line is determined only by the geometric length of the container and the parameters of the spectrograph and is independent of the conditions of reflection (see [9], for example). If the sample is irradiated inhomogeneously, then such a reflection will not eliminate completely the influence of the factor under consideration, although it reduces it to a minimum. Since a change in the reflection condition of the container appears only because of the inhomogeneity of its irradiation the effect of this factor should be investigated jointly with the second (the change in the behavior of the rays of the exciting light within the container). To do this, it is sufficient to investigate the concentration or temperature behavior of the line intensity for two radically differing incident light configurations. If the identical temperature (or concentration) dependence of the intensity is obtained for both methods of irradiation, then the second and fourth factors cannot be taken into account.

We measured the temperature dependence of the intensity of the 656 cm^{-1} line of carbon bisulfide in a single-tube elliptical irradiator and in an irradiator with a diffusor. As is seen from figure 3, the results obtained in these two series of measurements are in good agreement. Therefore, the second and fourth factors are not essential in our case.

Hence, the influence of the refractive index of the fluid in our apparatus appears only in terms of the change of the brilliance as the dispersed light leaves the container; it is proportional to n_f^2. In particular, the correction is $(1.67/1.36)^2 = 1.51$ for

* Such a high monochromator slit is usually used in the photoelectric method of recording that it is impossible to fulfill the above mentioned conditions of reflection for accessible fluid volumes. In these cases an additional factor arises which leads to the dependence of the fluxes being recorded on n_f. The Raman spectrum, reflected from the container walls [3,9,10], is incident precisely in the monochromator. An explanation of the role of this effect requires additional study.

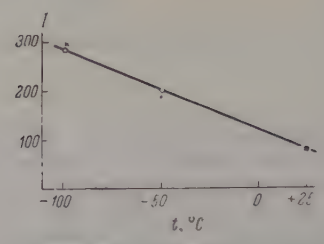


Figure 3. Temperature dependence of the intensity of the 656 cm^{-1} line of carbon bisulfide. Crosses - measurements in the elliptical illuminator; circles - measurement in an illuminator with a diffusor.

the measurement of the ratio of the alcohol and carbon bisulfide line intensities. It is essential that this correction is determined only by n_f and is independent of n_w. All the remaining factors do not lead to the necessity of introducing any kind of corrections.

It is understood that a somewhat different picture could be expected under other conditions. It is hardly probable, however, that the corrections would attain such magnitudes as have been obtained in [2]. In particular, it is stated in [2] that the correction to the attenuation of the exciting radiation because of the loss by reflection is compensated for $n_f < n_w$ by the change in the brightness of the scattered light as it leaves the container. According to our results, the first correction does not exceed 1% while the second can attain 25% (for $n_f = 1.35$). It is difficult to explain such a sharp disagreement between our results and those of [2]. It has not been excluded that it is related to inaccuracies in the theoretical computation performed in [2] without taking into account the reflection of the exciting light as it leaves the container, or to the faulty experimental method of measuring the loss by reflection, based on the assumption of the linearity of the concentration behavior of the line intensity in the solutions.

In conclusion, it is interesting to note that, at the temperature measurements when the line intensities refer to one molecule of the dispersing material, the correction to the change in the brightness of the scattered light as it leaves the container is compensated by the correction to the density d of the substance since n^2/d is independent of the temperature in practice.

The authors are greateful to P. A. Bazhulin for interest in the research and for discussions.

March 27, 1958

References

1. L.A. Woodward, J.H.B. George: Nature, 167, 193, (1951); Proc. Phys. Soc., B64, 780 (1951).
2. H. J. Bernstein, G. Allen: JOSA, 45, 237 (1955).
3. V. M. Pivovarov, Ia. S. Bobovich: Opt. i Spektr., 3, 134, (1957).
4. C. J. Carr, B. H. Zimm: J. Chem. Phys., 18, 1616 (1950).
5. J. J. Levinsons: JOSA, 41, 460(1951).
6. I. I. Fabelinskii: UFN, 63, 355, (1957).
7. G. S. Landsberg, P. A. Bazhulin, M. M. Sushchinski Fundamental Parameters of the Raman Spectra of Hydrocarbons (Osnovnye parametry spektrov kombinatsionnogo rasseianiia uglevodorodov), Moscow, 1956
8. G. G. Sliusarev: Geometric Optics (Geometricheskaia optika), Akad. Nauk Press, Moscow-Leningrad, 1954, p. 138.
9. S. G. Rautian: ZETF, 27, 625 (1954).
10. J. U. White, N. L. Alpert, A. G. DeBell: JOSA, 45, 154 (1955).

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

A Study Of The Concentration Extinction Of The Luminescence Of Dyes In Various Solutions And Isolation Of Various Types Of Extinction[1]

V. L. LEVSHIN AND E. G. BARANOVA

Abstract - In this paper we consider various forms of the transfer of excitation energy among molecules in concentrated solutions of luminescent substances, leading to extinction and depolarization of the luminescence. A distinction is made between the action of energy transfer from monomer to monomer and energy transfer from monomer to dimer or to higher polymers and these are distinguished from the process of inert absorption by non-luminescent combinations.

The development of these extinction processes is studied in a number of solutions corresponding to different degrees of association at a given level of concentration.

The transfer of excitation energy from one luminescent molecule to another plays an important role in many phenomena of luminescence. In the present paper we consider the transfer of energy to non-luminescent combinations, that is, transfers of energy leading to extinction of luminescence.

The concentration extinction of luminescence in solutions is a basic concentration effect, noticed in the earliest studies of luminescence. There are two modern lines of explanation of this phenomenon: one stresses the importance of reversible physico-chemical transformations taking place in the solution as the concentration is increased [1,2]; the other rests on a representation of extinction as a process of energy transfer from excited molecules to unexcited molecules of the same substance.

The significance of the formation of non-luminescent complexes, giving rise to inert absorption, was appreciated in the 1880's by Stenger and Walter; it has recently been re-asserted by one of the present authors [3,4] as an explanation of the extinction phenomenon.

The second, purely physical explanation arose from J. Perrin's hypothesis as to [5] the possibility of induction resonance between luminescent molecules of the same type. These ideas were developed by F. Perrin [6] and were taken as the foundation of a theory of extinction by Vavilov [7] and Galanin [8] . According to these authors, energy transfer from one monomer to another is accompanied by extinction in some fraction of its occurrences, but the cause of the extinction is not examined in detail. S.I. Vavilov, in his development of the theory, obtained expressions for the variation in luminescence, the duration of the excited state, and the polarization of the emitted light. The theory of energy transfer among monomers is in no position, however, to explain the dependence of the absorption spectrum of solutions on the solution concentration, or the increase in luminescence of solutions when they are heated, or the differences in the extinction curves observed when luminescence is excited by light of different wave lengths. Dushinskii [10] developed in 1937 a theory of these phenomena, based on the experimental data given in [3,4] and on the ideas of F. Perrin [9] concerning the transfer of energy to non-luminescent dimers. Since Dushinskii omitted the role of inert absorption and made a number of simplifications, his theory failed to yield the correct curves for concentration processes; nevertheless, as we shall see below, transfer of excitation energy to dimers does take place, and plays an important role in extinction processes.

In a paper by one of us [11] it was shown that extinction can arise in several ways, and that there are accordingly several types of concentration extinction. These can occur simultaneously, and in fact their joint occurrence is the general rule, rather than the exception; it is therefore necessary to isolate them for individual study.

In the present work we found methods for isolating the various extinction processes, so that it was possible to determine the relative importance of the several types under given definite conditions.

TYPES OF CONCENTRATION EXTINCTION AND METHODS FOR ISOLATING THEM

In an arbitrary solution at high concentration three superimposable extinction processes may occur:

1) Extinction by induction transfer of excitation energy from one monomer to another (Type I);

2) Extinction by transfer of excitation energy to dimers or higher complexes. When these complexes are non-luminescent, the transfer is accompanied by direct extinction; when they are luminescent, the transfer eliminates primary luminescence and substitutes the luminescence of sensitized complexes. (Type II);

3) Extinction by inert absorption, depending on the presence of non-luminescent complexes in the solution. The fraction of the light absorbed by luminescent monomers is then decreased, leading to a decrease in light output. (Type III)

The three types do not occur at the same concentration. The first depends on the monomer-monomer distance, i.e. on the absolute concentration of monomers. The second depends primarily on the monomer-dimer distance, i.e. it depends on the absolute dimer concentration. However, at low dimer concentrations, the concentration of monomers can also influence the rate of transfer from excited molecules to dimers, and can therefore influence the rate of extinction. (See below). Finally, the third type of extinction depends on the relative absorption capacity of the monomeric and dimeric components of the solution, i.e. on the ratio of the products of the concentration and absorption coefficients of the monomer, $\alpha_m C_m$, and the dimer, $\alpha_d C_d$.

ORDER IN WHICH THE EXPERIMENTS WERE CONDUCTED

The influence of the formation of non-luminescent aggregates was studied through a number of reversible physico-chemical reactions, and it was established that the observed concentration effects were not connected with changes in the degree of dissociation of the dyes, even though these changes

[1] Presented to the Sixth Conference on Luminescence February 19, 1958

induced sharp variations in the optical properties of the solution [12]. The addition of acids and alkalis to weak solutions sharply altered the pH of the solutions, and established the impossibility of attributing the observed concentration effects to the influence of pH.

The influence of polymers was determined by comparing the effects of heating dilute and concentrated solutions, with respect to the intensity of the luminescence. The flaring luminescence of concentrated solutions at high temperatures, or the much slower extinction of luminescence compared to the extinction rate of dilute solutions, indicated the existence of extinguishing polymers in concentrated solutions at low temperatures and the destruction of these by heating.

It was determined, by heating, whether the role of polymers is fundamentally that of acceptance of excitation energy by induction, or whether it also includes inert absorption of excited particles, as shown by the influence of the number of polymers present. In the first case the absorption spectrum would be essentially unchanged by an increase in concentration, whereas in the second case it would be significantly changed.

From the change in the absorption spectrum in certain cases it was possible to determine the degree of dissociation and also to make a quantitative distinction between transfer extinction and extinction by inert absorption. Our conclusions as to the relative importance of transfers of Types I and II were based on a comparison of the curves of concentration extinction in various solutions, favoring and hindering the formation of polymers.

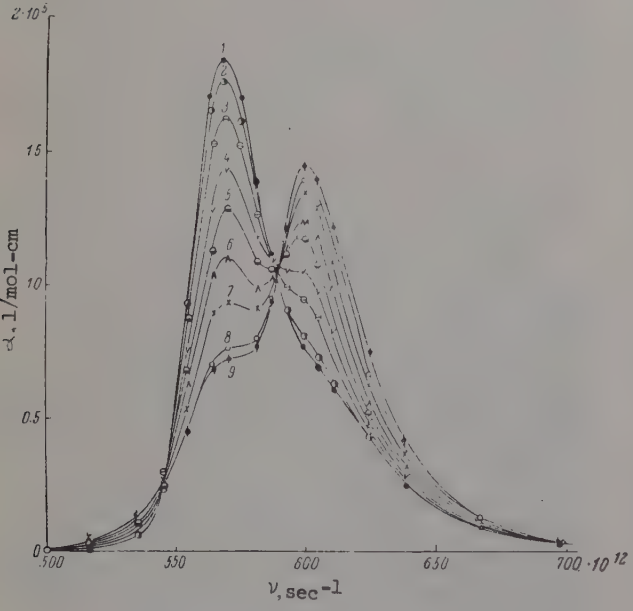


Fig. 1. Absorption spectra of aqueous solution of rhodamine 6J.

1 — $C = 4 \cdot 10^{-4}$, 2 — $C = 10^{-4}$, 3 — $C = 4 \cdot 10^{-5}$, 4 — $C = 10^{-4}$, 5 — $C = 2 \cdot 10^{-4}$, 6 — $C = 4 \cdot 10^{-4}$, 7 — $C = 10^{-3}$, 8 — $C = 2 \cdot 10^{-3}$, 9 — $C = 4 \cdot 10^{-3}$ mol/l.

Thus, the separation of the several types of concentration extinction was accomplished by: 1) study of the absorption spectrum; 2) study of the variations in intensity of luminescence of thin layers as a function of concentration; and 3) study of the effect of temperature on the output of light and on the form of the absorption spectrum.

Later we consider examples of the development of extinction in different solvents and develop the distinctions between the various types of extinction.

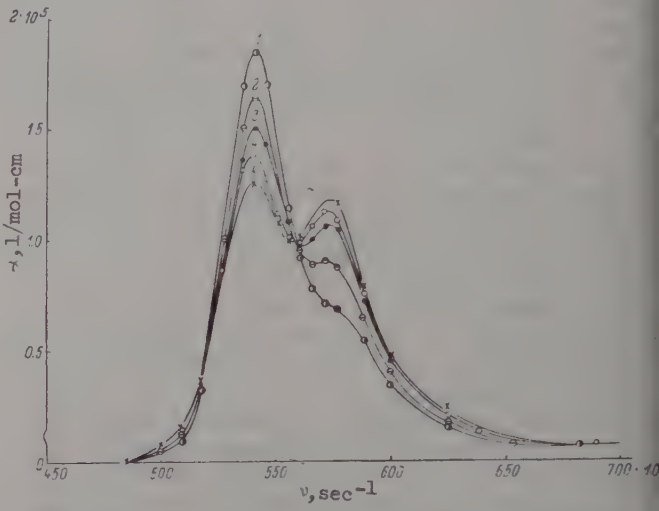


Fig. 2. Absorption spectra of aqueous solution of rhodamine 3B.

1 — $C = 4 \cdot 10^{-4}$, 2 — $C = 4 \cdot 10^{-4}$, 3 — $C = 10^{-3}$, 4 — $C = 2 \cdot 10^{-4}$, 5 — $C = 4 \cdot 10^{-4}$ mol/l.

AQUEOUS DYE SOLUTIONS

In concentrated aqueous solutions of dyes a large change in the absorption spectrum and a strong increase in the intensity of luminescence are observed as the temperature is raised to high levels. One of the authors, in his earliest investigations, attributed both effects purely to inert absorption by polymers. Förster [13] took this point of view with respect to rhodamines; however, the decrease in the duration of luminescence observed as the concentration is increased suggests that energy transfer occurs also. In [11], therefore, energy transfer to non-luminescent polymers was taken into account as well as inert absorption. In the present work, it has been possible to separate these two processes on the basis of experiments.

The absorption spectra of rhodamine 6J and 3B are presented in Figures 1 and 2 for various concentrations, ranging from 2×10^{-6} to 4×10^{-3} mol/l. In the region of low concentrations, up to 4×10^{-6} mol/l, the spectra are stable, and represent the absorption of monomers. This conclusion is supported by the close similarity of these spectra to the spectra of alcohol solutions (Fig. 3). Further increases in concentration lead to a gradual decrease in the long-wave maximum and a corresponding growth in the second short-wave maximum, characteristic of dimers but also present in rudimentary form in the spectra of monomers. In the ultraviolet region the absorption spectrum is stable throughout the range of concentrations so far investigated [14].

In calculating the degree of association in previous studies [4,14], it was assumed that the absorption curve for $C = 2 \times 10^{-3}$ gm/cm^3 corresponds to the spectrum of dimers. Since, however,

he very strong extinction of these solutions can e explained in part not only by the formation of on-luminescent polymers but also by transfer of xcitation energy to dimers, the assumption just tated is inexact and led to too high a value of he degree of association.

Table 1

hange in Association With Increase in Concentration or Rhodamine 6J and 3B in Aqueous Solution, and Growth in Extinction by Energy Transfer.

C mol/	Rhodamine 6J				Rhodamine 3B			
	x from absorption measurements.	J/CA	km/kd	τ/τ_0	x from absorption measurements.	J/CA	km/kd	τ/τ_0
·10⁻⁶	1	1	1	1	1	1	1	1
·10⁻⁵	0.95							
·10⁻⁵	0.92	0.90	1	1	0.98	1	1.02	1
·10⁻⁵	0.87	0.87	1	1	0.95	0.98	1.03	1
·10⁻⁴	0.72	0.74	1.02	1	0.90	0.91	1.01	1
·10⁻⁴	0.61	0.63	1.03	1	0.85	0.87	1.02	1
·10⁻⁴	0.50	0.52	1.04	0.8	0.74	0.76	1.02	0.93
·10⁻³	0.35	0.29	0.83	0.7	0.58	0.55	0.95	0.9
·10⁻³	0.26	0.17	0.67	0.6	0.46	0.33	0.72	0.8
·10⁻³	0.20	0.08	0.4	0.41	0.35	0.18	0.51	0.69
·10⁻³	0.18	0.05	0.3					
·10⁻³					0.28	0.08	0.29	
·10⁻³	0.14	0.02	0.14					

In this paper we determine the fraction of onomers from the absorption spectrum by using the eneral relations [4,15]

$$\alpha = \alpha_m x + \alpha_d (1-x), \qquad (1)$$

$$\frac{x^2}{1-x} = \frac{D}{C}, \qquad (2)$$

here and are respectively the coefficients f absorption as observed, as known for monomers, nd as known for dimers; D is the equilibribum onstant, and C the concentration.

It follows from (1) and (2) that

$$\frac{(\alpha - \alpha_d)^2}{\alpha_m - \alpha} = \frac{D}{C}(\alpha_m - \alpha_d), \qquad (3)$$

ince is obtained experimentally at the limit f low concentrations, there remain in equation 3) two unknowns, and D. To determine these e used the value of at a preselected wave length or two absorption spectra corresponding to two oderate concentrations for which the formation of igher polymers is improbable.

From two equations of the type of (3) we btain

$$\alpha_d = \frac{\alpha_1 - B\alpha_2}{1-B},$$

where

$$B = \sqrt{\frac{c_2(\alpha_m - \alpha_1)}{c_1(\alpha_m - \alpha_2)}}, \qquad (4)$$

C_1 and C_2 are the concentrations and α_1 and α_2 are he corresponding absorption coefficients. Knowing α_d and making use of (1) we calculate the degree of association for all concentrations for which the formation of higher polymers may be neglected. The calculations were carried out at the frequency of he monomer maximum. The computed values of the degree of association are given in Table 1.

The transition of a significant fraction of the molecules into the non-luminescent associated state is accompanied by the appearance of inert absorption and a corresponding decrease in the intensity of light emissions by the solution which must be taken into account in an investigation of energy transfer to dimers.

To distinguish transfer extinction from extinction as a result of inert absorption, the emission of luminescent solutions in thin layers was studied.

The intensity of emission of a thin layer of the solution is given by the expression

$$J = I\Delta\alpha_m Cxk_m k_d. \qquad (5)$$

where J is the observed emission intensity, I is the intensity of the exciting illumination at a specified wavelength, Δ is the thickness of the layer, α_m is the coefficient of absorption for monomers, C is the concentration of the solution, x the fraction of molecules in the monomeric state, as determined from absorption measurements, k_m is the coefficient of extinction for transfer of energy to monomers, k_d the coefficient of extinction for transfer to dimers. The product $I\Delta\alpha_m$ is denoted by A. We determined experimentally the curves of specific intensity diminution J/CA: curves 1 and 2,(Figs 4 and 5); Curve 3 shows the decrease in the fraction x of luminescent monomers; curve 4 shows the behavior of the transfer energy, the ordinate being the values of $k_m k_d$. We see that both types of extinction -- decrease in the fraction x of luminescent monomers and transfer of energy $k_m k_d$ -- produce effects of the same order of magnitude. The calculated decrease in energy output as a consequence of inert absorption for given x is expressed by the equation

$$B' = \frac{\alpha_m x}{\alpha_m x + \alpha_d (1-x)}. \qquad (6)$$

With regard to the relative values of the coefficients k_m, k_d for extinction by transfer of energy to monomers and dimers, we offer the following remarks: In alcohol solutions no extinction is observed at concentrations less than 10^{-2} mol/l, so that one should not expect energy transfer from monomer to monomer in alcohol solutions at concentrations less than 10^{-2} mol/l. The maximum concentration in aqueous solutions was in fact 10^{-2} mol/l. We may therefore assume that in aqueous solutions $k_m = 1$ at all concentrations attainable in practice. The weak effect of energy transfer among monomers is due in part (1) to the fact that the overlap of the spectra of emission and absorption of monomers is about one-half the overlap of the emission spectrum of monomers with the absorption spectrum of dimers and (2) to the fact that at high concentrations the number of dimers in the solution is greater than the number of monomers. The basic cause of the absence of extinction by energy transfer among monomers is, however, not the low probability that the transfer will occur, but rather the low probability that it will cause extinction when it does occur.

As indicated earlier, a parameter fundamental to the development of transfer extinction is the distance between the excited molecules and the non-luminescent polymers. This distance, in

semi-extinguished aqueous solutions of rhodamine 6J and 3B, turns out to have the values 100 and 85Å, respectively.

According to the transfer theory, extinction by transfer induces a shift in the wavelength of the emitted light which should be proportional to the output. In order to test this hypothesis, direct measurements of the wavelength of the emitted light were made at several different concentrations, using an L.A Tumerman fluorometer. As may be seen from the values of τ/τ_0 presented in Table 1, the mean emitted wavelength does indeed vary in proportion to the product $k_m k_d$. Since in aqueous solutions of rhodamine the extinction mechanisms of Types II and III develop simultaneously, it was necessary to investigate these types in solutions in which one or the other predominated.

Examples of solutions in which Type I predominates -- i.e. extinction by transfer from monomer to monomer--are not known to us. It is possible that uranyl sulfate dissolved in sulfuric acid is such an example [16, 17] .

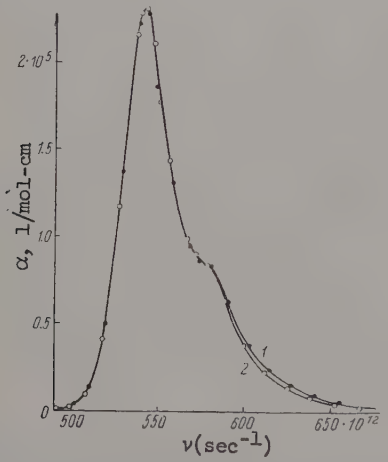


Fig. 3. Absorption spectra of aqueous and alcohol solutions of Rhodamine 3B at low concentrations ($C = 2 \times 10^{-6}$ mol/l).

1 - aqueous solution
2 - alcohol solution (the aqueous solution spectrum was adjusted to the scale of the alcoholic spectrum and the frequency shift was 2 mμ toward the short wavelength region)

ALCOHOL AND GLYCERINE SOLUTIONS OF RHODAMINE 6J AND 3B

Ethyl alcohol and glycerine are similar with respect to many properties, but differ sharply in viscosity. They are excellent solvents for rhodamines. The concentration of dye in solution can be brought up to values as high as 0.16 mol/l . Heating a concentrated extinguished alcohol solution leads to flaring emission, which plainly points to the important role played by high polymers in this process (see Fig. 6).

In glycerine solutions there is a strong flaring of emission upon heating of concentrated solutions (Fig. 7) and at the same time a significant change in the absorption spectrum (Fig. 8), which enables us to calculate the degree of dimerization of the solution (Table 2) by comparing it with the spectra of aqueous solutions.

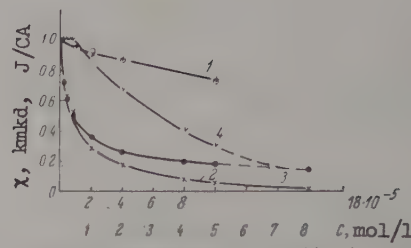


Fig. 4. Ratio of emission intensity to concentration in thin layers of aqueous solutions of Rhodamine 6J as concentration is increased.
Increase in Concentration =
1 - from 4×10^{-6} to 10^{-4} mol/l
2 - from 4×10^{-5} to 8×10^{-3} mol/l
3,4 show separately the extinctions due to inert absorption and energy transfer, respectively.

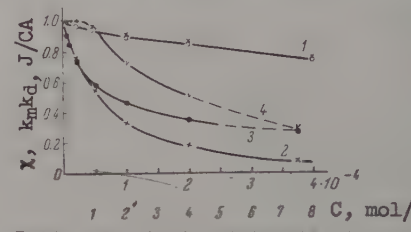


Fig. 5. Ratio of emission intensity to concentration in thin layers of aqueous solutions of Rhodamine 3B as concentration is increased.

Increase in concentration
1 - from 2×10^{-6} to 4×10^{-4} mol/l;
2 - from 5×10^{-4} to 5×10^{-3} mol/l;
3,4 show separately the extinctions due to inert absorption and energy transfer, respectively.

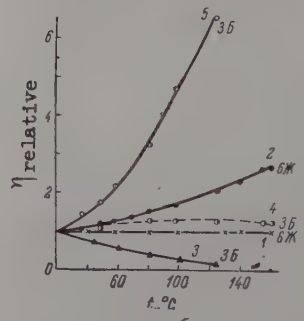


Fig.6.

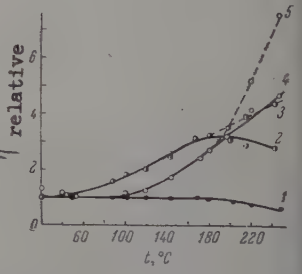


Fig.7.

Fig. 6. Temperature dependence of the luminescent output of alcohol solutions of rhodamine 3B and 6J ($\lambda_{exc.}$ = 365 mμ).

1,3 - $C = 3 \times 10^{-4}$, 2, 4, 5, - $C = 1.6 \times 10^{-1}$ mol/l,
5 - data corrected for temperature extinction (thin layers).

Figure 7. Temperature dependence of the output of glycerine solutions of rhodamine 6J (λ_{exc} = 365 mμ)
1 - $C = 1 \cdot 10^{-4}$ mol/l ; 2,3 - $C = 2 \cdot 10^{-2}$ mol/l ;
4,5 - $C = 8 \cdot 10^{-2}$ mol/l ; 3, 5 are corrected for temperature extinction (thin layers)

Table 2

Development of Transfer Extinction With Increase in Concentration of Rhodamine 6J in Glycerine Solution.

C mol/l	x from absorption	Decrease in output	$k_m k_d$	N/cm^3	N_d/cm^3
10^{-4}	1	1	1		
10^{-2}	0.97	0.4	0.4	$0.6 \cdot 10^{19}$	$0.9 \cdot 10^{17}$
10^{-2}	0.92	0.11	0.12	$1.2 \cdot 10^{19}$	$4.8 \cdot 10^{17}$
10^{-2}	0.89	0.02	0.02	$2.4 \cdot 10^{19}$	$1.32 \cdot 10^{18}$
10^{-2}	0.54	0.01		$4.8 \cdot 10^{19}$	$1.1 \cdot 10^{19}$

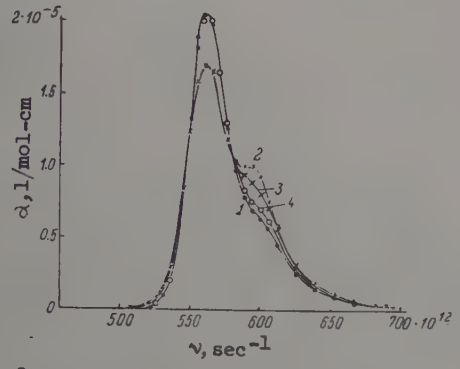


Fig. 8. Absorption spectra of glycerine solution of rhodamine 6J.

$1 - C = 10^{-3}$; $2 - C = 2 \cdot 10^{-2}$; $3 - C = 10^{-2}$; $4 - C = 4 \cdot 10^{-2}$ mol/l.

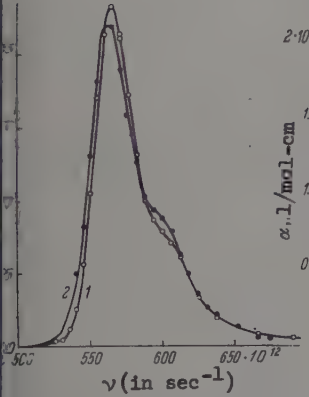


Fig. 9. Absorption spectra of alcohol solution of rhodamine 6J.

$C = 4 \cdot 10^{-4}$; $2 - C = 8 \cdot 10^{-3}$ mol/l.

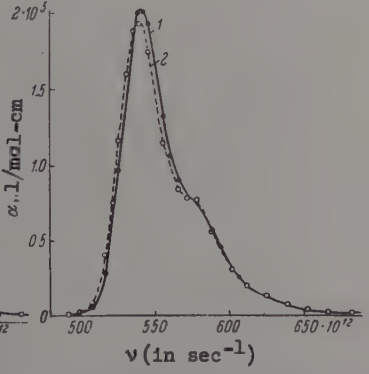


Fig. 10. Absorption spectra of alcohol solution of rhodamine 3B.

$1 - C = 2 \cdot 10^{-2}$; $2 - C = 8 \cdot 10^{-3}$ mol/l.

In Figures 9 and 10 are shown the absorption spectra of rhodamine 6J and 3B in ethyl alcohol solution at both low and high concentrations. With an increase in concentration the spectra of the alcohol solutions change very little. By comparing these spectra with the spectra of aqueous solutions we may conclude that in alcohol solutions of rhodamine 3B there are about 5% polymers at $C = 8 \times 10^{-2}$ mol/l ; it must be noted, however, that the character of the shift in the absorption spectra in alcohol solutions is somewhat different from that of the shift in aqueous solutions.

So long as the polymers constitute only an insignificant fraction of the molecules in the solution, the process of extinction by inert absorption cannot be significant, and extinction must occur primarily through transfer of energy to dimers (Fig. 11). The question of the role of transfer of energy among monomers was considered earlier. Such transfer must occur, since the absorption and emission spectra coincide; nevertheless no extinction was observed in alcohol solutions at concentrations up to 10^{-2} mol/l ; accordingly, in this region of concentrations extinction by energy transfer among monomers is negligibly small, although the presence of transfer is shown [18,19] by the depolarization of the emitted light in glycerine solutions. Depolarization begins to set in at concentrations as low as 10^{-4} mol/l . On this basis we may regard alcohol solutions (up to 4×10^{-2} mol/l as solutions in which extinction occurs almost exclusively by transfer of energy to dimers. Because of the excellent solubility of dyes in alcohol and the very high total concentration of strong alcoholic solutions, even a small fraction of polymers corresponds to a high concentration of them, leading to extinction.

Also of interest is the question whether there occurs a transfer of energy from an excited monomer directly to a dimer, or whether some intermediate transfers to monomers are required. This latter possibility is certainly not excluded, since monomer receiving energy from another monomer may in turn pass it on to a dimer. There is a significant difference between the degrees of extinction of aqueous and alcohol solutions at the same dimer concentration, and it may be that the mechanism just mentioned is responsible for this difference.

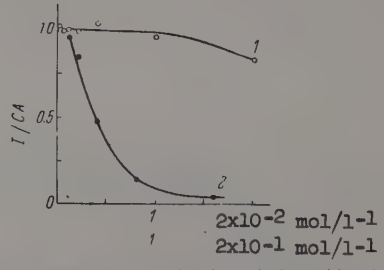


Figure 11. Ratio of emission intensity to concentration in thin layers of alcohol solutions of rhodamine 3B for increases in concentration from $C = 10^{-4}$ to $2 \cdot 10^{-2}$ mol/l (1) and from $C = 1 \cdot 10^{-2}$ to $16 \cdot 10^{-1}$ mol/l (2)

CONCENTRATION EXTINCTION OF DYES IN ELECTROLYTIC SOLUTIONS

Concentration extinction due to inert absorption appears in its purest form when polymers exist at low concentrations. In this case the percentage content of polymerized molecules will be large, even though the absolute concentration is low; therefore we may expect a large shift in the absorption spectrum and a correspondingly strong extinction by inert absorption, while the mean distance between monomers and polymers remains large, and extinction by energy transfer is therefore practically nonexistent. A suitable example can be found in solutions of dyes in electrolytes. We carried out experiments with rhodamine 6J in a 5% NaCl solution,

and found support for the assumptions just stated. The degree of association was determined on the one hand by comparison of the forms of the absorption spectra with the absorption spectra of extinguished aqueous solutions, and on the other hand by the change in the intensity of emission under the assumption that transfer to dimers does not exist.

It follows from Table 3 that extinction in electrolytic solutions occurs almost completely through inert absorption.

Table 3

Polymerization of Rhodamine 6J (1-x) in Electrolytic Solution (Water +5% NaCl).

Method of determination \ C, mol/l	$4 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
By absorption	0.08	0.14	0.22	0.33	0.46
By luminescence	—	—	0.21	0.28	0.44

CONCLUSIONS

1. In concentrated solutions of luminescent substances, extinction of emission is composed basically of extinction by transfer of excitation energy from monomers to non-luminescent polymers and of extinction by inert absorption. These modes of extinction have differing degrees of relative importance in differing substances, and depend on the properties of the solvent; the possibility of isolating them therefore exists.

2. The transfer of energy from monomer to monomer leads to extinction of emission only in highly specialized circumstances; such transfers therefore do not normally lead to direct extinction, but they can influence the extinction process by providing an intermediate state in the transfer of energy from excited monomers to dimers. Energy transfer from monomer to monomer leads to depolarization of the emitted light.

3. Transfer of energy from luminescent monomers to non-luminescent polymers plays an important role in the development of concentration extinction. This type of extinction can be studied quantitively in both aqueous and alcohol solutions.

4. An important role in the development of extinction is played by the decrease in luminescence that accompanies the process of inert absorption by non-luminescent polymers which develop in the solution. It is especially important in solvents with low dissolving power. Inert absorption is easily detected by noting the strong change in the absorption spectrum in concentrated solutions.

The authors wish to express their thanks to L. V. Krotova for carrying out some of the experiments and assisting in the work, and to O.V. Shalaeva for measuring the duration of emission of the solutions

24 March 1958

References

1. F. Stenger: Wied. Ann., 28, 201 (1886).
2. B. Walter: Wied. Ann., 34, 316 (1886).
3. V. L. Levshin: Zs. f. Phys., 43, 230 (1927).
4. V. L. Levshin: Zh. Fiz. Khim., 6, 1 (1935).
5. J. Perrin: 2 cons. de chim. Solvay, 322 (1925); CR, Acad. des Sciences, 184, 1097 (1927).
6. F. Perrin: Ann. de phys., Ser. 10, vol. 17, 283 (1932).
7. S. I. Vavilov: ZETF, 13, 13 (1943).
8. M. D. GALANIN: ZETF, 28, 485 (1955) (See Sov. Phys. JETP).
9. F. Perrin: C.R., 192, 1727 (1931).
10. F. Dushinskii: DAN USSR, 14,-73, (1937) DAN USSR, 17, 179 (1937).
11. V. L. Levshin: IAN USSR, Phys. ser., 20, 397 (1956) (see Bulletin, Phys. ser., 20, 362 (1956 translated by Columbia Tech. Trans.).
12. V. L. Levshin: IAN USSR, Phys. ser., 20, 419 (1956) (See Columbia Tech. Trans. Bulletin).
13. Th. Foerster: Fluoreszenz organischer Verbindungen. Vandentroick and Ruprecht, Gottingen, 1951.
14. V. L. Levshin, E. G. Baranova: IAN USSR, 20, 42 (1956) (see Bulletin of Col. Tech. Trans.).
15. T. P. Kravets, A. L. Peskina, Z. V. Zhidkova: IAN USSR, Phys. ser., 14, 493 (1950).
16. S. I. Vavilov, V. L. Levshin: Zs. f. Phys., 48, 397 (1928).
17. V. L. Levshin IAN USSR, Phys. ser., 2, 185 (193
18. N. D. Zhevandrov: DAN USSR, 100, 455 (1955).
19. M. D. Galanin: Tr. FIAN USSR, 5, 539 (1950).

M VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar' , 1959
L. VI, No. 1 OPTICS AND SPECTROSCOPY January , 1959

On The Fluorescence Law In Polystyrene On Excitation By Electrons

S. F. KILIN AND I. M. ROZMAN

Abstract; It is shown with the help of a monochromatic fluorometer with a modulated electron beam that scintillations in polystyrene do not decay according to a simple exponential law. The results obtained contradict the theory of Birks and agree satisfactorily with the assumption of the essential role of bimolecular quenching in the scintillation process.

A study of the kinetics of luminescence of organic scintillators with excitation by ionizing particles is of great interest both for their practical utilization as fast detectors of radiation and for the clarification of the mechanism of these scintillations. Although the experimental data on luminescence decay [1-3] was obtained by different methods, their interpretation is usually based on the assumption of an exponential law of fluorescence. Thus, for example, in the most direct - oscillographic method the average luminescence lifetime is determined by the fall-off region of the oscillogram. The rising part is due to parasitic impedances of the recording apparatus.

Experimental attempts at the clarification of the fluorescence law of crystalline anthracene were undertaken in [4, 5]. The results obtained were diverse. The author of [4] came to the conclusion that in the first instant of time a rapid decay of the luminescence intensity takes place which thereafter goes over to an exponential decay. The author of [5] concluded that in anthracene an increase in the luminescence intensity takes place at the beginning of the process, which goes over to an exponential decay.

EXPERIMENTAL RESULTS

We have investigated the luminescence of polystyrene, which is used as a base in the preparation of plastic scintillators [6]. The luminescence lifetime was determined with the help of a phase fluorimeter with a modulated (30 kv) electron beam [7]. The measured delay of the luminescence phase with respect to the phase of the exciting radiation is determined by the relation

$$\tan\varphi = \frac{\int_0^\infty l(t)\sin\omega t dt}{\int_0^\infty l(t)\cos\omega t dt}, \qquad (1)$$

where $l(t)$ is the luminescence decay law and ω is the modulation frequency of the exciting radiation. In the exponential law case the decay of the "fluorometric" time

$$\tau_{fl} = \frac{1}{\omega}\operatorname{tg}\varphi$$

does not depend on ω and coincides with the average luminescence lifetime τ. This affords an easy verification of the exponential character of the fluorescence law by measuring φ for different ω[8].

In the non-optical excitation of luminescence the problem arises of determining the zero of the fluorometer[7]. For many instruments this problem may be easily solved if there are two different scintillators with exponential fluorescence laws (where τ_1 and τ_2 are unknown) or one scintillator with a known τ. We tested several pairs of solid organic scintillators, and also NaI(Tl) in combination with polystyrene. In no case were we successful in obtaining a qualitative correspondence between the experimental results and the assumption of an exponential fluorescence law for even one of the scintillators. We therefore applied the following method for the determination of the phase angle of polystyrene. The difference between the phase angle for pure polystyrene φ_{10} and that of the plastic scintillators composed of polystyrene with added triphenylpyrazoline (or tetraphenylbutadiene) φ_2 was measured for each frequency ω, i.e.,

$$\Delta\varphi = \varphi_{10} - \varphi_2$$

Moreover, the phase angle of the same additive φ_{20} was measured during its direct excitation by light in the polystyrene-transparent band. It was found that for sufficiently high concentrations of the additive ($C \geq 0.06$ gm/gm) the angle $\Phi = \Delta\varphi + \varphi_{20}$ does not depend on C(table 1), which corresponds to the condition $\varphi_2 = \varphi_{20}$. This must occur if the quantum yield of the nonradiative transfer of the excitation energy from polystyrene to the additive is close to unity. Direct measurements confirmed that for the systems examined this condition is fullfilled*. Since Φ, moreover, does not even depend on the nature of the luminescing additive, then one must reckon that the phase angle for polystyrene

$$\varphi_{10} = \Phi$$

Table 1.

Dependence of the phase angles on the concentration of the luminescing substance (C) and the modulation frequency (ω) (angles given degrees of arc)

Luminescent Material	C, gm/gm	$\omega = 0.502 \times 10^8$ sec^{-1}			$\omega = 0.754 \times 10^8$ sec^{-1}			$\omega = 0.942 \times 10^8$ sec^{-1}			$\omega = 1.26 \times 10^8$ sec^{-1}		
		$\Delta\varphi$	φ_{20}	Φ	$\Delta\varphi$	φ_{20}	Φ	$\Delta\varphi$	φ_{20}	Φ	$\Delta\varphi$	φ_{20}	Φ
1,3,5-triphenylpyrazoline - Δ^2	0.06	17.3	13.6	30.9	18.9	19.9	38.7	17.1	24.3	41.4	17.0	31.1	48.1
	0.10	16.8	13.2	30.0	19.3	19.3	38.6	16.9	23.7	40.6	17.2	30.3	47.5
1,1,4,4-tetraphenylbutadiene-1,3	0.06	20.9	8.4	29.3	28.4	11.0	39.4	—	—	—	28.7	20.6	49.3
$\tan\Phi$		0.58			0.81			0.87			1.12		
$\tau_{fl} = \frac{1}{\omega}\tan\Phi$ (x10^9 sec.)		11.5 ± 0.4			10.7 ± 0.4			9.2 ± 0.3			8.9 ± 0.3		

The average values for τ_{fl} for polystyrene are adduced in the last line of table 1. It is evident that τ_{fl} depends on ω, i.e., the luminescence of polystyrene on excitation by electrons does not decay according to exponential law.

* Detailed results will be given in a separate work.

DISCUSSION OF THE RESULTS OBTAINED

The decrease τ_{fl} with an increase of ω contradicts the theory of radioluminescence propounded by Birks [1, 9] according to which increase of τ_{fl} with ω would have been expected. In connection with this we shall proceed from the assumption that in the process of scintillation there exists an interaction of the excited molecules with each other, leading to a partial quenching of the fluorescence [10, 11]. Since the bimolecular quenching depends on the local concentration of the excited molecules, it is necessary to take into account the spatial distribution of excitation produced by the exciting electrons. Qualitatively one may assume that a certain number of excitations produced by the primary and fast secondary electrons are distributed in such a way that they are isolated from the others, and that the remaining activated molecules are located in clusters [12]. In order to simplify the following calculations, which have a qualitative character, it is assumed that all clusters are identical. Then the kinetics of the change of the number of excited molecules in both groups is determined by equations

$$\frac{dn}{dt} = -\lambda n,$$

$$\frac{dn_c}{dt} = -\lambda n_c - \frac{\beta}{a_c N_0} n_c^2$$

with the initial conditions: at t = 0, n = αN_0, $n_c = \alpha_c N_0$. Here N_0 is the total number of excitations produced by one electron during its deceleration in the scintillator, α and α_c give the portion of isolated excitations in clusters, $\tau = 1/\lambda$ is the average lifetime of the excited state of the molecule, β is a constant characterizing the speed of the bimolecular quenching in clusters of the given dimension*.

The solution has the form

$$N(t) = n + n_c = N_0\left[\alpha e^{-\lambda t} + \alpha_c \frac{\lambda/\beta}{(1+\lambda/\beta)\, e^{\lambda t} - 1}\right]. \tag{2}$$

The magnitude of the scintillations or the number of emitted photons calculated for one exciting particle (without taking reabsorption into account) is

$$S = \int_0^\infty k_e N(t)\, dt = \frac{k_e}{\lambda} N_0\left[\alpha + \alpha_c \frac{\lambda}{\beta} \ln\left(1 + \frac{\beta}{\lambda}\right)\right],$$

where k_e is the probability of emission of a photon by the excited molecule. Since according to the definition of the quantum yield of fluorescence

$$\eta_f = \frac{k_e}{\lambda},$$

and the quantum yield of the scintillations

$$\eta_s = \frac{S}{N_0}$$

then

$$\eta_c = \eta_f\left[\alpha + \alpha_c \frac{\lambda}{\beta} \ln\left(1 + \frac{\beta}{\lambda}\right)\right]. \tag{3}$$

In the work [14] it was shown that the temperature quenching of the luminescence of polystyrene over a wide temperature interval does not depend on the nature of the exciting radiation, i.e.

$$\frac{\eta_c}{\eta_f} = \text{const.} \ (\pm\ 5\%) \tag{4}$$

Relation (4) is fulfilled during a change of η_f (i. e., λ) by a factor of 3, which is possible either in the case $\alpha_c \ll \alpha$, or in the case of a very weak dependence of the quantity $\lambda/\beta \ln(1 + \beta/\lambda)$ on The first possibility is excluded. Indeed, from sufficiently general considerations it follows that in the excitation of one molecule of polystyrene on the average an energy of about 8 eV is spent by the ionizing particle [15]. This implies that in the absence of additional quenching the energy yield of the scintillations is*

$$V_c = \frac{3.8}{9}\eta_f = 0.5\ \eta_f$$

(3.8 eV is the average photon energy in the polystyrene spectrum). For Co^{60} gamma-rays experiment [16] gives the significantly lower magnitude

$$V_c = 0.11\ \eta_f$$

Consequently, about 80% of the excited molecule undergo additional damping. In accordance with formula (3) this gives

$$\alpha \leqslant 0.2 \text{ and } \alpha_c \geqslant 0.8,$$

and on the basis of (4) we obtain $\beta/\lambda \geqslant 100$.

However, one may assume that a certain portion of the primary activations do not lead to the excitation of the "fluorescent" state of the molecule [17], i.e., besides the bimolecular quenching there exists a type of "instantaneous quenching" The presence of such a quenching affects our estimates; instead of (3) it is necessary to write

$$\eta_c = \delta\eta_f\left[\alpha + \alpha_c \frac{\lambda}{\beta}\left(\ln\left(1 + \frac{\beta}{\lambda}\right)\right)\right].$$

Since $\eta_c/\eta_f = 0.2$, then

$$\delta\left[\alpha + \alpha_c \frac{\lambda}{\beta} \ln\left(1 + \frac{\beta}{\lambda}\right)\right] \approx 0.2 \tag{5}$$

with $\alpha + \alpha_c = 1$.

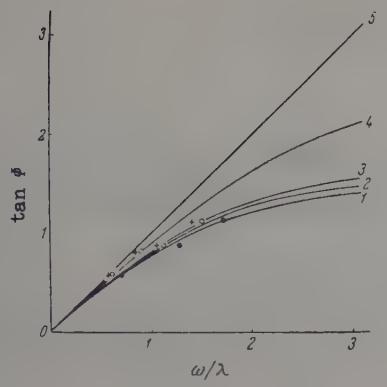
The relation (5) together with condition (4) allows the estimation of the quantities α, α_c, and β/λ in their dependence on the quantity δ (table 2).

Table 2

δ	β/λ	α_c	Curve No. in the figure
1.0	100	0.84	1
	1000	0.80	—
0.75	60	0.77	2
	100	0.75	—
	1000	0.72	—
0.50	30	0.68	3
	100	0.63	4
	1000	0.60	—
0.20	—	0	5

* It is easily seen that we do not distinguish between excited and ionized molecules. This is admissible for a solid medium, since the recombination of a positive ion with an electron takes place in approximately 10^{-11} sec [13].

* Editor's Note: Believe $V_c = \frac{3.8}{8}\eta_{f=0.5}\eta_f$ instead of $\frac{3.8}{9}\eta_f$ as given in the paper.



Dependence of the phase angle on the modulation frequency Experimental points: dark circles - for $\lambda = 7.2 \cdot 10^7$ sec^{-1}, light circles - $\lambda = 8.4 \cdot 10^7$ sec^{-1}, crosses - $\lambda = 9 \cdot 10^7$ sec^{-1}.

In the figure are adduced the results of calculating tan Φ according to formula (1) with the fluorescence law (2). The corresponding values of the parameters are given in table 1. It is easily seen that the experimental results agree satisfactorily with the assumption that bimolecular quenching is present. Since the steepness of the curves of (tan Φ, ω/λ) increased with a decrease of δ, (curves 1, 2, 3, 5) or on an increase of β/λ (curves 3 and 4), then one may assume that $\delta > 0.5$ and $\beta/\lambda \approx 10^2$.

However, it is necessary to remark that the experimental data do no contradict the other assumption either, namely: there are several components in polystyrene whose fluorescence decays according to exponential laws with various γ. Additional investigations are necessary for a complete solution of this question.

February 13, 1958

References

1. J. BIRKS: Scintillation Counters, Foreign Literature Publishing House, Moscow, 1955.
2. R. K. SWANK and W. L. BUCK: Rev. Sci. Instr. 26, 15 (1955).
3. R. C. SANGSTER and J. W. IRVINE: J. Chem. Phys. 24, 670 (1956).
4. G. T. WRIGHT: Proc. Phys. Soc. B69, 358 (1956).
5. F. GLOSER: Z. Naturforschung 11a, 1030 (1956).
6. ANDREESHCHEV et al., Prib. i tekhn. eksper. 1, 32 (1956).
7. KILIN, PAVLOV and ROZMAN, Prib. i tekhn. eksper. 1, 50 (1956).
8. L. A. TUMERMAN: Uspekhi fiz. nauk 33, 218 (1947).
9. J. B. BIRKS: Phys. Rev. 94, 1567 (1954).
10. BROSER et al., Z. Naturforschung 3a, 6 (1948).
11. G. T. WRIGHT: Phys. Rev. 91, 1282 (1953).
12. D. E. LEA: Actions of Radiations on Living Cells, Cambridge, 1946.
13. A. H. SAMOEL and J. L. MAGEE: J. Chem. Phys. 21, 1080 (1953).
14. I. M. ROZMAN: Opt. i spekt. 2, 480 (1957).
15. I. M. ROZMAN: Dissertation, Sukhumi, 1957.
16. E. A. ANDREESHCHEV and I. M. ROZMAN: Opt. i spekt. 5, 39 (1958).
17. M. D. GALANIN and A. P. GRISHIN: Zhur. eksp. i teor. fiz. 30, 33 (1956).

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

Effect of Reabsorption on the Fluorescence Lifetimes of Organic Substances

S. F. KILIN AND I. M. ROZMAN

Abstract: With the help of a monochromatic phase fluorometer it is shown that the fluorescence of tetraphenylbutadene and triphenylpyrazoline in polystyrene decays according to an exponential law in the presence of considerable reabsorption. The results of measuring the average luminescence lifetime, the fluorescence spectra and the quantum yield agree with the calculations.

The partial overlapping of the molecular absorption and emission spectra leads to the absorption of a certain portion of the fluorescence quanta within the macroscopic phosphor, and thus to the appearance of secondary fluorescence. As a result of the fluorescent quantum yield, the fluorescent spectrum and rate of luminescence decay depends on the degree of reabsorption. Several methods for calculating the influence of reabsorption on the fluorescence lifetime have been proposed [1-5]. The most general method, based on the solution of the kinetic equation for the density of the excited luminescence centers, was developed in [5].

Our investigations are concerned with the radiation kinetics of the luminescence of plastic scintillators with a polystyrene base [6] during excitation by ionizing radiation. It is evident that the last stages of the scintillations appear from the radiation of the excited molecules of the luminescing additive contained in these scintillators. Therefore it is valuable to establish the dependence of the average fluorescence lifetimes of the additives on their concentrations. The results obtained in [1-5] are not directly applicable for the solution of this problem, since in the works mentioned the case of a semi-infinite phosphor is considered, which automatically excludes the concentration dependence.

METHOD

We applied a method for calculation analogous to the method used in calculating the role of secondary fluorescence in [1].

Let the luminescing substance possess the following molecular characteristics: a quantum yield of fluorescence η_0, an average lifetime of the excited state τ_0, and a quantum emission spectrum $f_0(\nu)$. The probability of absorption of a photon ν within the phosphor depends on the absorption coefficient χ_ν, and the path length of the photon in the phosphor. Consequently, the degree of reabsorption depends on the spatial distribution of the excited molecules. Let us introduce the quantities $r_j(\nu)$ equal to the average absorption probability of a photon ν for a certain definite spatial distribution of the excited molecules $n_j(r)$. The number of such molecules in the whole volume of the phosphor is

$$N_j = \int_V n_j dV$$

The total number of excited phosphor molecules at a certain moment of time t is made up of the sum of the primary molecules, directly excited by the external radiation; the secondary molecules, excited by the fluorescence of the primary molecules; the tertiary molecules, excited by the secondary molecules, etc. The rate of change of the number of primary molecules N_1 is determined by the strength of the external excitation (A photons/sec) and by the rate of deactivation ($\lambda_0 = 1/\tau_0$). The change in the number of secondary molecules occurs because of the deactivation and absorption of the primary fluorescence. The fraction of absorption here is

$$\int r_1(\nu) f_0(\nu)\, d\nu.$$

However, not all of the absorption events lead to the excitation of molecules. If we assume that the decrease of the quantum fluorescence yield in the anti-Stokes region is explained by the existence of ineffective absorption [7], then the fraction of effectively absorbed photons ν will be $\eta(\nu)/\eta_0$, where $\eta(\nu)$ is the molecular quantum fluorescence yield on excitation by the frequency ν. Thus, for the determination of N_j we obtain the following system of equations.*

$$\left.\begin{aligned} &\frac{dN_1}{dt} + \lambda_0 N_1 = A, \\ &\frac{dN_j}{dt} + \lambda_0 N_j = \lambda_0 R_{j-1} N_{j-1} \ (j \geqslant 2), \end{aligned}\right\} \qquad (1)$$

where

$$R_j = \int \tau_1(\nu)\, r_j(\nu)\, f_0(\nu)\, d\nu.$$

Equation (1) may be put into the form

$$D^m N_m(\vartheta) = \frac{1}{\lambda_0} P_{m-1} A(\vartheta), \qquad (2)$$

where

$$\vartheta = \lambda_0 t,$$

the operator

$$D = \frac{d}{d\vartheta} + 1,$$

and

$$P_k = R_0 R_1 \ldots R_k \ (R_0 = 1).$$

The general solution of (2) is

$$N_{m+1}(\vartheta) = e^{-\vartheta} \left\{ \sum_{k=0}^{m} C_{m+1,k} \vartheta^k + \frac{P_m}{\lambda_0} \int_0^{\vartheta} \frac{(\vartheta - x)^m}{m!} e^x A(x)\, dx \right\}. \qquad (3)$$

The constants $C_{j,k}$ are inter-related by the system (1) and are defined by the initial conditions and by the choice of ν_0 (arbitrary).

We shall consider the following particular cases.

1. At the moment $t = 0$ an instantaneous (impulsive) absorption of N_0 photons from the external source takes place, i.e.,

$$A(t) = N_0 \delta(t),$$

* It is assumed that the average path length of protons for which $r(\nu) \neq 0$ is small, i.e., $1/c \ll \tau_0$, where c is the velocity of light in the phosphor.

here $\delta(t)$ is the δ-function. Transforming to the variable ϑ, we have

$$A(\vartheta) = \lambda_0 N_0 \delta(\vartheta).$$

Taking account of the initial conditions $N_{m+1}(0) = 0$, we obtain from formula (3)

$$N_{m+1}(t) = N_0 P_m \frac{(\lambda_0 t)^m}{m!} e^{-\lambda_0 t} \qquad (1.4)$$

The luminescence intensity

$$L(t) = \lambda_0 \tau_0 \sum_{m=0}^{\infty} N_{m+1}(t)(1 - \bar{r}_{m+1}),$$

where

$$\bar{r}_j = \int r_j(\nu) f_0(\nu)\, d\nu.$$

The fluorescence decay law is

$$l(t) \equiv \frac{L(t)}{L(0)} = e^{-\lambda_0 t} \sum_{m=0}^{\infty} \frac{1 - \bar{r}_{m+1}}{1 - \bar{r}_1} P_m \frac{(\lambda_0 t)^m}{m!}. \qquad (1.5)$$

Hence, in the presence of reabsorption the luminescence does not decay, generally speaking, according to an exponential law.

The external (fluorescence) yield is

$$\eta_{ext} = \frac{1}{N_0} \int_0^{\infty} L(t)\, dt$$

or

$$\eta_{ext} = \eta_0 \sum_{m=0}^{\infty} (1 - \bar{r}_{m+1}) P_m. \qquad (1.6)$$

Finally, the fluorescence spectrum, averaged over time, will be

$$f_{ext}(\nu) = f_0(\nu) \sum_{m=0}^{\infty} [1 - r_{m+1}(\nu)] P_m. \qquad (1.7)$$

2. The exciting radiation is switched on with constant intensity A at t = 0. The initial conditions are $N_{m+1}(0) = 0$. Formula (3) gives

$$N_{m+1}(t) = \frac{AP_m}{\lambda_0} \left[1 - e^{-\lambda_0 t} \sum_{k=0}^{m} \frac{(\lambda_0 t)^k}{k!} \right]. \qquad (2.4)$$

Hence the luminescence growth law is easily found to be

$$l_{growth}(t) = \tau_0 \left[B_0 - e^{-\lambda_0 t} \sum_{k=0}^{\infty} B_k \frac{(\lambda_0 t)^k}{k!} \right], \qquad (2.5)$$

where

$$B_k = \sum_{m=k+1}^{\infty} (1 - \bar{r}_m) P_{m-1}.$$

Consequently, the secondary luminescence increases the time to build up the stationary state [4]. This time is the smaller, the faster P_m decreases with increasing m, i. e., the smaller the quantum yield and the reabsorption.

In the stationary state the number of molecules in the different excitation groups is determined by formula (2.4) for t = ∞ or directly from (2)

$$N_{m+1,0} = \frac{A}{\lambda_0} P_m. \qquad (2.6)$$

In this case the fluorescence yield and luminescence spectrum are determined by the formulas (1.6) and (1.7) obtained earlier.

3. If on reaching the stationary state an external excitation is switched on (at t = 0), then the kinetics of the subsequent luminescence is determined by equation (2) with A=0 and with the initial conditions (2.6)

$$N_{m+1}(\vartheta) = e^{-\vartheta} \left[N_{m+1,0} + \sum_{k=1}^{m} C_{m+1,k} \vartheta^k \right]$$

With the aid of equation (1) it is easy to show that

$$C_{m+1,k} = \frac{A}{\lambda_0} \frac{P_m}{k!}.$$

Consequently,

$$N_{m+1}(t) = \frac{A}{\lambda_0} P_m e^{-\lambda_0 t} \sum_{k=0}^{m} \frac{(\lambda_0 t)^k}{k!} \qquad (3.4)$$

and the fluorescence decay law becomes

$$l(t) = \frac{1}{B_0} e^{-\lambda_0 t} \sum_{k=0}^{\infty} B_k \frac{(\lambda_0 t)^k}{k!}, \qquad (3.5)$$

i.e., in the general case it is not an exponential law, as for impluse excitation.

The experimental data (see below) indicate the fact that for the plastic scintillators we investigated the fluorescence decay of the additives follows an exponential law with good precision. It is easily shown that (1.5) and (3.5) lead to an exponential if we assume the average absorption probabilities for all "generations" of photons are identical, i. e., if we take

$$r_1(\nu) = r_2(\nu) = \ldots = r(\nu).$$

In this case all the R_j are also equal and

$$P_m = R^m.$$

Since $R < 1$, one obtains from (1.6) and (1.7)

$$\eta_{ext} = \eta_0 \frac{1 - \bar{r}}{1 - R}, \qquad (8)$$

$$f_{ext.} = f_0(\nu) \frac{1 - r(\nu)}{1 - R}. \qquad (9)$$

One obtains from (1.5) and (3.5) for the decay law

$$l(t) = e^{-\lambda_0 t(1-R)},$$

i.e., the average luminescence lifetime in the presence of absorption and secondary emission is

$$\tau = \frac{\tau_0}{1 - R}. \qquad (10)$$

Finally, the luminescence growth law (2.5) also acquires a simple form

$$l_{growth}(t) = \eta_{ext}(1 - e^{-t/\tau}). \qquad (11)$$

Formulas (8) - (10) lead to some simple relations between the yield, spectrum and luminescence lifetime. It is experimentally easy to measure the quantity

$$F(\nu) = \text{const}\, f_{ext}(\nu)$$

If we choose the arbitrary factor such that $F(\nu) = f_0(\nu)$ for the long wavelength part of the spectrum, then it follows from (9) that

$$f_0(\nu)\, r(\nu) = f_0(\nu) - F(\nu) \qquad (12)$$

and

$$1 - \bar{r} = \int F(\nu)\, d\nu \equiv S. \qquad (13)$$

Then a simple relation is obtained from (8) and (10) between the yield and the lifetime

$$\frac{\eta_{ext}}{\eta_0} = S \frac{\tau}{\tau_0}, \qquad (14)$$

which is open to experimental verification. Further, if the magnitude of the relative quantum yield $\eta(\nu)/\eta_0$ is known, then (12) allows the calcu-

lation of the quantity $\sigma = R/\eta_0$. From formula (10) we obtain

$$\eta_0 = \frac{1-\tau_0/\tau}{\sigma}, \qquad (15)$$

i.e., a relation for the determination of the molecular quantum yield [3].

EXPERIMENTAL RESULTS

The average fluorescence lifetime was determined in our phase fluorometer with a modulated electron beam [8]. The fluorescence of the luminescent additives was excited by the luminescence of a polystyrene disk of 1 mm thickness, placed directly on the scintillator under investigation (fig. 1). The front surface of the disk was covered by a layer of aluminum (by evaporation) of about 300 μ thickness. The (30 kV) accelerating system gave a wide beam, which made possible obtaining a sufficient luminescence intensity in the polystyrene without noticeably damaging it [9]. Specially conducted experiments showed that under the influence of a large dose of ionizing radiation not only a decrease of the light yield occurred, but also the luminescence lifetime of polystyrene decreased, therefore the polystyrene disks were measured by us before and after each series of experiments. Under the conditions of our experiments τ for polystyrene remained constant. The revolving holder (4; fig. 1) had 8 sockets, which made possible the rapid measurement of 6 samples (one socket for determining the zero and one for adjusting the apparatus before the measurements). The neutral filter 6 with continuously variable density guaranteed the possibility of measuring a constant value of the electric signal at the input of the electronic circuit independently of the fluorescence yield and the luminescence spectrum of the samples.

Fig. 1.

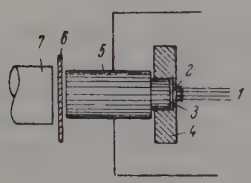


Fig. 1. The excitation and recording of fluorescence in measurements of the luminescence lifetimes. 1 - electron beam; 2 - polystyrene disk; 3 - scintillator; 4 - holder; 5 - light-pipe; 6 - neutral filter; 7 - photomultiplier, type FEU-25

As is well known, the luminescence phase lag with respect to the phase of the exciting radiation, modulated by a frequency ω, is determined by the formula

$$\tan\varphi = \frac{\int_0^\infty l(t)\sin\omega t\,dt}{\int_0^\infty l(t)\cos\omega t\,dt},$$

where $l(t)$ is the luminescence decay law. The quantity

$$\tau_{fl} \equiv \frac{1}{\omega}\operatorname{tg}\varphi$$

is called the fluorometric luminescence lifetime [10]. If the decay law is exponential with an average luminescence lifetime τ, then

$$\tau_{fl} = \tau$$

independently of ω. Conversely, if τ_{fl} does not depend on ω, then the decay law may be considered exponential. In this connection the circuit of our fluorometer [8] was supplemented by special attachments which allowed measurements to be made at frequencies of 20, 15, 12 and 8 mc.

In fig. 2 are presented results of measurements of τ_{fl} for plastic scintillators with various concentrations of 1,1,4,4-tetraphenylbutadene-1,3 (4PB) and 1,3,5-triphenylpyrazoline- Δ^2 (3PP). It is easily seen that within the limits of precision of the measurements τ_{fl} does not depend on ω, i.e., the fluorescence law is exponential. Here the average luminescence lifetime increases substantially with the concentration of the luminescent substance (fig. 3).

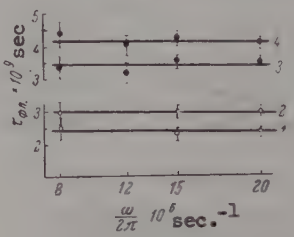


Fig. 2 τ_{fl} for several ω.
1 - $3\cdot10^{-4}$ gm/gm 4PB;
2 - $6\cdot10^{-2}$ gm/gm 4PB;
3 - $1.4\cdot10^{-4}$ gm/gm 3PP; 4 - 0.2 gm/gm 3PP.

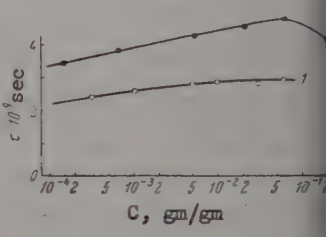


Fig. 3 Average fluorescence lifetime dependence on concentration of luminescent substance.
1 - 4PB; 2 - 3PP.

In accordance with the calculations presented above, it follows from the results obtained that the degree of reabsorption weakly depends on the spatial distribution of the excited molecules. This conclusion is not an unexpected one. In the overlapping region of the absorption and emission spectra the absorption coefficients of both substances investigated change very rapidly with wavelength. Thus, for the scintillators with 3PP in the 405-450 mμ wavelength region we obtained

$$k_\lambda = 5.9\cdot10^4\,\frac{c}{1+c}\cdot10^{-\frac{\lambda-400}{11.4}}\ \text{см}^{-1},$$

i.e., k_λ changes by a factor of 10 on a change in λ of 11.4 mμ. k_λ changes even faster for 4PB. Since the width of the emission band is considerably greater than 10 mμ (figs. 4 and 5), the variation in the spatial distribution of the radiating molecules weakly influences $\bar{r}$. With the geometry of our experiments (fig. 1) this influence is significantly lowered, first, because of the large width of the samples (10 mm), and second, because of the poor optical contact between the sample and the light-pipe and the absence of contact between the light-pipe and the photocathode of the photomultiplier. Only about 10% of the emitted photons could pass through the front sur-

iface of the samples (the refractive index was 1.66) tthe remaining photons could emerge only after multtiple reflections.

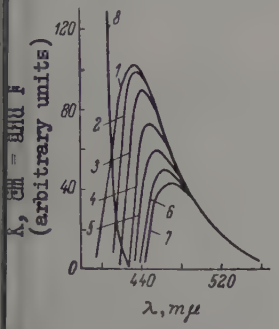


Fig. 4 Fluorescence spectra of 3PP in polystyrene.
1 - Molecular luminescence spectrum, concentration of 3PP (in gm/gm): 2 - $1.4 \cdot 10^{-4}$; 3 - $1 \cdot 10^{-3}$; 4 - 0.01; 5 - 0.03; 6 - 0.1; 7 - 0.2; 8 - absorption coefficient for a concentration of 0.01 gm/gm.

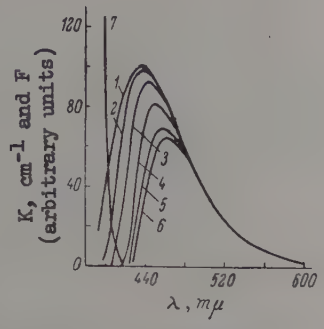


Fig. 5 Fluorescence spectra of 4PB in polystyrene.
1 - Molecular luminescence spectrum, concentration of 4PB (in gm/gm): 2 - $1 \cdot 10^{-4}$; 3 - $1 \cdot 10^{-3}$; 4 - 0.01; 5 - 0.03; 6 - 0.66; 7 - absorption coefficient for a concentration of 0.01 gm/gm.

Degree of Fluorescence Reabsorption for 3PP and 4PB

C, gm/gm	$1 - \bar{r}$	
	3PP	4PB
$1 \cdot 10^{-4}$	0.87	0.91
$1 \cdot 10^{-3}$	.75	.80
$1 \cdot 10^{-2}$	.60	.66
$3 \cdot 10^{-2}$	.52	.59
$6 \cdot 10^{-2}$	.47	.54
$1 \cdot 10^{-1}$	.43	
$2 \cdot 10^{-1}$	.37	

For the quantitative verification of formulas (10) and (14) the luminescence spectra and relative fluorescence yields were measured in the apparatus described in [11]. The geometry was the same as in fig. 1 (except for the polystyrene disk). The luminescence spectra are presented in figs. 4 and 5, and the results of the calculation of $\bar{r}$ according to formula (13) are presented in the table*. Results of the measurement of the luminescence intensity before (1) and after (2) the introduction of the corrections for the spectral sensitivity of the photomultiplier [11] are presented in fig. 6.

According to formula (14), the quantity

$$q \equiv \frac{\eta_{ext}}{\tau(1-\bar{r})} = \frac{\eta^0}{\tau_0}$$

must not depend on the concentration of the luminescent substance. Making use of the data of figs. 3 and 6 and the table it is easy to convince oneself that they are in accord with the experimental data (fig. 7). The absolute value of q, presented in fig. 7, was obtained in the following manner. According to the known η_0 [6] and the measured τ, τ_0 was calculated under the assumption $\eta(\nu) = \eta_0$. For concentrations of additives $C < 10^{-2}$ gm/gm, the τ_0's thus obtained did not depend on C and were equal to 3.13 ± 0.07 for 3PP and 2.17 ± 0.09 for 4PB.

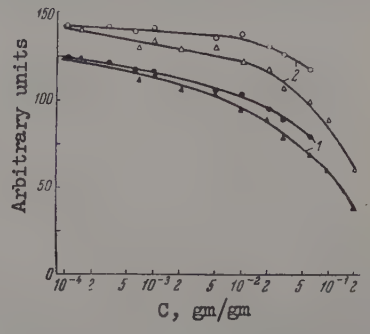


Fig. 6 Dependence of the external fluorescence yield on the concentration of the luminescent additives.
1 - photomultiplier current = 19; 2 - relative external quantum yield, dark and light circles - dark and light triangles - 3PP.

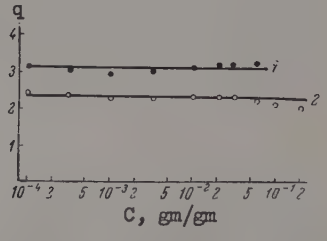


Fig. 7 Dependence of the quantity q on the concentration of the luminescent substance.
1 - 4PB; 2 - 3PP

AT high 3PP concentration a decrease of τ (fig. 3) and a still more rapid decrease of η_{ext} (figs. 6 and 7) took place. This was due to two causes. Firstly, it was due to concentration quenching, which was verified by the decrease of the degree of fluorescence polarization with an increase in concentration. Secondly, for $C > 3 \cdot 10^{-2}$ gm/gm an additional quenching at the surface layer of the phosphor takes place. It is easy to convince oneself about this if one compares the intensity of fluorescence for excitation by $\lambda = 366$ mμ ($\varkappa = 1.3 \cdot 10^5$ cm²/gm and $\lambda = 405$ mμ ($\varkappa = 1.9 \cdot 10^4$ cm²/gm). In the second case the intensity decreases more slowly with an increase in concentration ($> 3 \cdot 10^{-2}$ gm/gm).

No data exist in the literature relative to the fluorescence lifetime of 3PP. For 4PB in polystyrene an increase of τ_{fl} from $2.5 \cdot 10^{-9}$ sec for C = 0.001% to $2.8 \cdot 10^{-9}$ sec for C = 3% was found. The latter number is found to be in satisfactory agreement with our results. The oscillographic measurement of the average luminescence lifetime of

* The molecular luminescence spectra were obtained by measuring on the excitation side in samples of thickness 0.5 mm and with a luminescent substance concentration of 10^{-4} gm/gm.

our [6] plastic scintillators with $1.5 \cdot 10^{-2}$ gm/gm 4PB in polystyrene under excitation by fast neutrons gave $\tau_{sc} = 5.0 \pm 0.5 \cdot 10^{-9}$ sec. for samples ϕ 22 and h 20 mm*. This number coincides well with other data for plastics with 4PB [13]. A small increase of the luminescence lifetime on excitation by ionizing radiation in the present case is apparently connected with the rate of energy transfer. Detailed results of the investigations of the kinetics of scintillations in plastics will be expounded in a separate paper.

February 13, 1958

* Private Communication from G. A. Vasil'ev and V. M. Gorbachev.

References

1. M. D. GALANIN: Tr. FIAN USSR 5, 339 (1950).
2. J. B. BIRKS and W. A. LITTLE: Proc. Phys. Soc. A 66, 921 (1953).
3. G. T. WRIGHT: Phys. Soc. B 68, 241 (1955).
4. A. P. IVANOV, Opt. i Spektr. 2, 800 (1957).
5. V. M. AGRANOVICH: Opt. i Spektr. 3, 84 (1957).
6. E. A. ANDREESHCHEV: Prib. i tekh. eksper. No. 1, 32 (1956).
7. B. I. STEPANOV: Liuminestsentsiia slozhnykh molekul (The Luminescence of Complex Molecules) Publishing house of the Academy of Science of the Belorussian SSR, 1955.
8. KILIN, PAVLOV and ROZMAN: P i TE No. 2, 50 (1956).
9. I. M. ROZMAN and K. G. TSIMMER: Atomnaia energiia 2, 54 (1957) (Translation exsists by CB)
10. M. D. GALANIN: Zhur. eksper. i teor. fiz. 28, 485 (1955)
11. E. A. ANDREESHCHEV and I. M. ROZMAN: Opt. spektr. 2, 488 (1957).
12. KOTON ET AL.: Prib. i tekh. eksper. No. 1, 49 (1957).
13. R. K. SWANK: Uspekh. fiz nauk 58, 519 (1956).

TOM VI, Vyp. 1
TOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

Measurements of the Optical Constants of Copper, Gold and Nickel in the Infrared Region of the Spectrum

I. N. SHKLIAREVSKII AND V. G. PADALKA

Abstract: With the help of a previously developed method, [4] [5] measurements have been made of the indexes of refraction μ and absorption $\mu\chi$ of thick films of copper, gold and nickel, prepared by vacuum evaporation, in the region of 1-12 μ. Using the measured values of the optical constants, values are determined for the concentration of conduction electrons N, the relaxation time τ, and the conductivity σ_0. These values are compared with those found in earlier work [6] [9]. The absorption coefficients A are calculated for the region 1-12 μ.

INTRODUCTION

The complex dielectric constant of a metal equals

$$\tilde{\varepsilon} = \varepsilon - i\frac{4\pi\sigma}{\omega} = [\mu - i(\mu\chi)]^2. \quad (1)$$

Here ϵ is the dielectric constant, σ is the conductivity, μ and $\mu\chi$ are the indexes of refraction and absorption, and ω is the angular frequency. On the basis of the classical theory of free electrons, Drude [1] derived formulas for the dependence of the real and imaginary parts of the dielectric constant on frequency, concentration of free electrons N, and $\nu_0 = \frac{1}{\tau}$, where τ is the relaxation time.

$$\varepsilon = \mu^2 - (\mu\chi)^2 = 1 - \frac{4\pi Ne^2}{m(\omega^2 + \nu_0^2)}, \quad (2)$$

$$\sigma = \frac{\mu(\mu\chi)\omega}{2\pi} = \frac{Ne^2\nu_0}{m(\omega^2 + \nu_0^2)}, \quad (3)$$

where e and m are the charge and mass of the electron. In the limit where $\omega \to 0$, $\sigma \to \sigma_0$

$$\sigma_0 = \frac{Ne^2}{m\nu_0} = \frac{Ne^2\tau}{m}. \quad (4)$$

The dispersion formulas of Drude are valid for a model of free electrons obeying the laws of quantum mechanics. [2] The free electron model holds for frequencies less than ω_0, which corresponds to the threshold of the internal photo-effect. For many metals ω_0 lies in the visible or near infra-red region of the spectrum. Hence for $\lambda >$ 4-5 μ the optical properties of many metals are determined by the formulas of the free electron theory. This allows one to calculate N, τ and σ_0 from measurements of the optical constants μ and $\mu\chi$. Recently Dingle [3] has extended the dispersion relations to take account of the anomalous skin effect.

RESULTS OF THE MEASUREMENTS OF μ AND χ

The optical constants of copper, gold, and nickel were measured with the help of a method worked out previously [4] [5]. Measurements were made on several pairs of samples, and in each case gave highly reproducible values of μ and $\mu\chi$. The results of the measurements are given in Tables 1, 2 and 3. In the various columns are listed the values of the wavelength λ, the angles of incidence φ of the light on the samples, the number of reflections m, the phase differences Δ, the azimuthal angles ψ, and the indexes of refraction μ and absorption $\mu\chi$. The optical constants are calculated from the formulae:

$$\mu = \sin\varphi \operatorname{tg}\varphi \frac{\cos 2\psi}{1 - \sin 2\psi \cos\Delta} \quad (5)$$

$$\mu\chi = -\sin\varphi \operatorname{tg}\varphi \frac{\sin 2\psi \sin\Delta}{1 - \sin 2\psi \cos\Delta}. \quad (6)$$

1. Copper. Thick layers of copper were deposited on glass plates by vacuum distillation from two molybdenum boats, arranged so that the thicknesses of the films on both glass plates were almost entirely uniform. It took five days to measure the optical constants in the region from 1-12 μ. Control measurements were made on freshly prepared samples, about 4-5 hours after their preparation; that time was necessary to adjust the mirrors and to measure φ and ψ for the given wavelength. These control measurements gave the same values of the optical constants as the measurements on samples prepared five days before measurement. This means that by the time the measurements were made, the growth of the oxide film on the copper has already ceased (or very nearly). The influence of the oxide film on the values of the results was not taken into account. According to the approximate calculations of Hodgson, [6] an oxide layer of 0.01 λ changes the effective value of the optical constants μ and $\mu\chi$ by no more than a few percent.

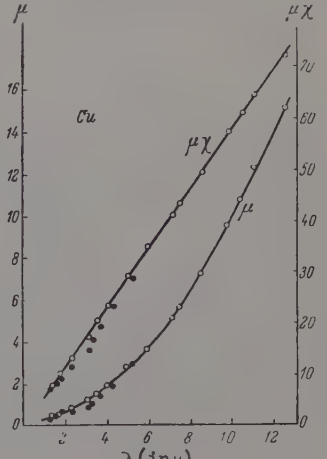


Fig. 1.

The results of the measurements are given in Table 1. In Figure 1, we have compared our values (open circles) with the values of Forsterling and Freedericksz [7] (solid circles).

2. Gold. Gold films of 1.5-2 μ thickness were deposited on glass plates by vacuum distillation from two molybdenum boats, arranged as in the previous case. For the first pair of samples, the measurements of the optical constants were made during the seven days immediately after their preparation. Measurements on the second pair of samples were made a month after their preparation. The results coincided extremely well with those

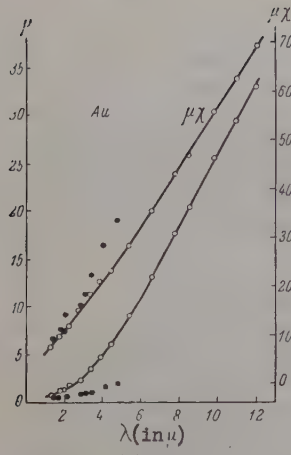


Fig. 2.

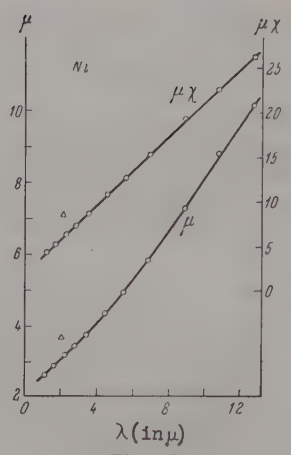


Fig. 3.

Table 1.

λ	φ	m	−Δ	ψ	μ	μχ
1.35	77°48′	3	60°	43°35′	0.45	7.81
1.69	80 18	3	60	43 33	0.58	9.96
2.28	82 30	3	60	43 26	0.82	13.0
3.00	80	5	36	43 48	1.22	17.1
3.4	81 30	5	36	43 44	1.53	20.3
3.97	82 30	5	36	43 35	1.94	23.1
4.87	84	5	36	43 20	2.86	28.9
5.8	85	5	36	43 12	3.71	34.6
7.0	85 45	5	36	42 50	5.25	40.7
7.3	86	5	36	42 45	5.79	43.2
8.35	86 30	5	36	42 31	7.28	49.2
9.6	87	5	36	42 08	9.76	57.2
10.25	86	7	25 43	42 45	11.0	60.6
10.8	86 15	7	25 43	42 34	12.6	64.3
12.25	86 40	7	25 43	42 20	15.5	71.9

Table 2.

λ	φ	m	−Δ	ψ	μ	μχ
1.3	77°	3	60°	42°39′	0.69	7.26
1.75	80	3	60	42 09	1.1	9.59
1.95	81	3	60	42	1.3	10.7
2.26	76	5	36	42 41	1.62	11.8
2.8	79	5	36	42 35	2.2	15.3
3.43	81	5	36	41 51	3.49	18.6
3.95	82 15′	5	36	41 20	4.71	21.5
4.55	80	7	25 43′	41 48	5.95	23.0
5.5	82	7	25 43	41 02	9.05	28.2
6.65	82	9	20	41 27	12.9	35.5
7.9	85	7	25 43	40	17.6	43.2
8.65	85 30	7	25 43	39 46	20.2	47.4
9.9	87 20	5	36	37 34	25.2	55.9
11.1	86 40	7	25 43	39 19	29.0	62.5
12.1	87	7	25 43	39 15	32.4	69.2

Table 3.

λ	φ	m	−Δ	ψ	μ	μχ
1.12	73°	3	60°	30°58′	2.63	4.28
1.58	75	3	60	31 54	2.89	5.08
2.18	77	3	60	32 54	3.18	6.13
2.72	78 30′	3	60	33 40	3.44	7.15
3.4	80	3	60	34 36	3.72	8.49
4.4	81 48	3	60	35 13	4.35	10.59
5.4	78	5	36	38 27	4.92	12.4
6.75	80	5	36	38 37	5.86	15.2
8.7	82	5	36	38 42	7.31	19.2
10.5	80 30	7	25 43′	40 09	8.86	22.5
12.5	81 45	7	25 43	40 12	10.2	26.2

found for the first pair of samples. The results for gold are given in Table 2. In Figure 2 we have compared our values for the optical constants of gold (open circles) with those found in reference [7]. The agreement is not so good as for the case of copper.

3. Nickel. The thick nickel films were deposited on glass plates by evaporation from three fine tungsten wires of .8 mm diameter, bent into loops and suitably arranged around the glass plates. Nickel had been electrolytically deposited previously on the tungsten wires. Upon heating the tungsten wires with an electric current, the nickel melted and collected in the bends of the loops in the form of small droplets. The evaporation process was stopped when about half of the melted nickel had evaporated. The nickel was electrolytically deposited on the tungsten in the following bath:

nickel sulfate	30.0 gm.
sodium chloride	0.3
boric acid	0.6
distilled water	100 .0

The bath temperature was 20°C. The current density was 8.5 ma/cm^2. The deposition of the nickel lasted 15 - 20 hours. The tungsten wires had been cleaned previously in a 20% solution of sodium hydroxide, at a temperature of 60-70°C, followed by a thorough washing in distilled water. The results for the optical constants of nickel are given in Table 3. In Figure 3 our measurements of $\mu = f(\lambda)$ and $\mu\chi = \varphi(\lambda)$ curves (circles) are compared with the values μ and $\mu\chi$ for $\lambda = 2\mu$ measured by Ingersoll [8] (triangles).

DETERMINATION OF N, τ and σ_0

In the spectral region satisfying the inequality

$$\nu_0^2 \ll \omega^2 \ll \omega_0^2, \tag{7}$$

the following relation derived from equation (2) is valid

$$(\mu\chi)^2 - \mu^2 + 1 = \frac{4\pi N e^2}{m\omega^2}. \tag{8}$$

This relation holds for the case of anomalous as well as normal skin effect. [2] Hence equation (8) allows one to determine the concentration of free electrons N from the measured values of μ and $\mu\chi$. This is assuming that m is the mass of a free electron. We note that according to Kaganov, [9] m in equation (8) is the effective mass, and hence it is more proper to determine the ratio N/meff rather than N from equation (8). For convenience in comparing the results with those of other authors [6] [10] we present values of N; the values of N/m_{eff} can be obtained by a simple conversion.

If the optical constants of a metal are measured in a spectral region satisfying equation (7), then it follows from equation (8) that N will be a constant under the condition that

$$(\mu\chi)^2 - \mu^2 + 1 = f(\lambda^2) \tag{9}$$

or, what is the same

$$\lg[(\mu\chi)^2 - \mu^2 + 1] = f(\lg\lambda) \tag{10}$$

should be straight lines. With the aid of either of these straight lines it is not difficult to define the concentration of free electrons.

Knowing the concentration of free electrons then using equation (3), and the inequality (7) ke may determine the relaxation time τ. Here : are assuming a normal skin effect. It is easy » see that

$$\lg \frac{\mu(\mu\chi)}{\lambda} = \varphi(\lg\lambda) \quad (11)$$

ast have the form of a straight line, and with ae aid of that line one may define the quantity $= \frac{1}{\nu_0}$. The lines (11) and (10) will be parallel. ay deviation of (10) or (11) from a straight line ndicates, that in the given region of the spec- rum, the free electron theory is not valid.

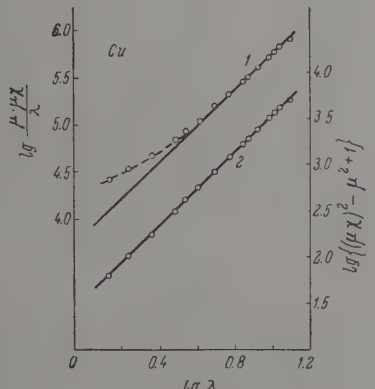


Fig. 4.

In figures 4, 5, and 6 we show the relations 10) and (11) for the cases of copper, gold and ickel. "Number 1" refers to equation (11), and number 2" to equation (10). In the short wavelen- th region of the spectrum, the experimental points or copper and gold deviate from the straight line $\log \frac{\mu(\mu\chi)}{\lambda} = \varphi(\lg\lambda)$. For the case of nickel, the ex- erimental points of the curve $\log \frac{\mu(\mu\chi)}{\lambda}$ do not lie n a straight line anywhere in the region investi- ated (from 1-12μ).

Using equation (4) we may define the conduc- ivity σ_0 from the values found for N and τ. ere we are assuming that the relaxation time, found y the method described above, is the same as for he case of a static field.

Table 4.

$N_a \cdot 10^{-22}$ cm^{-3}	$N \cdot 10^{-22}$ CM^{-3}			$\tau \cdot 10^{15}$ sec.			$\sigma_0 \cdot 10^{-16}$ CGSunits			
	this work	[9]	[10]	this work	[9]	[10]	this work	[9]	[10]	bulk conductivity
8.5	3.8 *	5.2	3.5	14	7.4	14.1	13.5	9.7	15.4	58
5.9	7.2	6.4	5.4	14.2	14.4	17.5	26	23.1	23.4	61
5.9	2.8	3.1	—	5	17.7	—	3.6	13.6	—	44
9.1	0.4 **	—	1.3	7.2	—	10.2	0.76	—	3.16	13.7

If, according to ref.[12], we put m* = 1.47m, then $N = 5.57 \cdot 10^{22}$ cm^{-3}.

If, according to ref.[12], we put m* = 28m, then $N = 11.2 \cdot 10^{22}$ cm^{-3}.

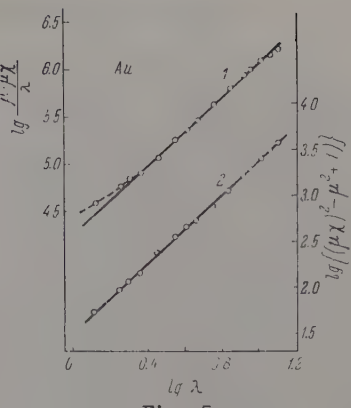


Fig. 5.

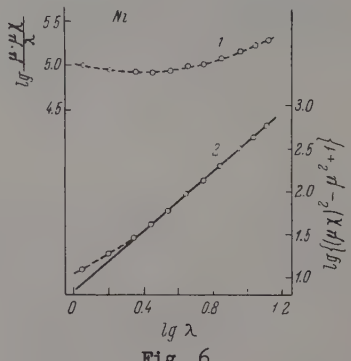


Fig. 6.

In Table 4, we give the values for N, τ and σ_0, for copper, silver, gold and nickel, computed from the measurements of the optical constants μ and $\mu\chi$. The optical constants of silver are taken from a previous article [5]. In the same table, for purposes of comparison, we have tabulated the values for N, τ and σ_0, calculated by an analogous method from the measurements of Hodgson [6], Beattie and Conn [10]; we also give the density of atoms per cubic centimeter N_a and the bulk conductivity of these metals, measured at constant current, σ_0 mass [11]. For the case of nickel τ was calculated from μ and $\mu\chi$ for $\lambda = 12.5\,\mu$. One should note the very satisfactory agreement between our values for N, τ and σ_0 with those in references [6] and [10]. Unfortunately it was impossible to make an analogous comparison for the optical constants μ and $\mu\chi$. In our opinion it is very unfortunate that the authors cited did not quote their values for μ and $\mu\chi$.

DETERMINATION OF THE ABSORPTION COEFFICIENT A

Along with the optical constants μ and $\mu\chi$, the absorption coefficient A is of great importance in the description of a metal. Usually the absorption coefficients of metals are measured by a calorimetric method, but they may be calculated also from known values of μ and $\mu\chi$. In fact,

$$A = 1 - R = \frac{4\mu}{(\mu+1)^2 + (\mu\chi)^2}, \tag{12}$$

where R is the coefficient of reflection. For a more precise definition of A it would be necessary to smooth out the scatter of the experimental values for the optical constants. The values of μ and $\mu\chi$ substituted in (12) were found from the corresponding curves in figures 1-3. The dependence of the absorption coefficients on wavelength in the region 1-12 μ for copper, silver, [5] gold and nickel are given in figure 7. Vertical axis I refers to copper, silver and gold, and vertical axis II refers to nickel. Our values for the absorption coefficients A are somewhat higher than the values measured by the calorimetric method (see, for example, reference [2]).

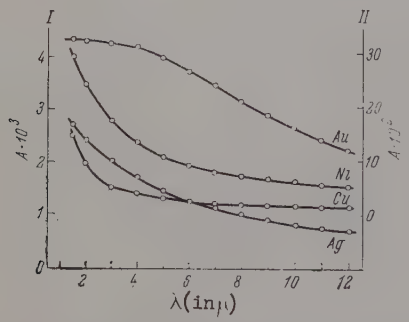


Fig. 7.

The rather high values of A for gold are related, in our opinion, to the high values of μ which we found (due perhaps to insufficiently clean samples).

In conclusion, the authors express their deep thanks to Prof. K. D. Sinel'nikov for his continued interest in this work.

March 24, 1957.

References

1. P. Drude: Ann. d. Phys., 14, 936, (1904).
2. V. L. Ginzburg, G. P. Motulevich: UFN, 55 467, (1955).
3. R. B. Dingle: Physica, 19, 311, 348, (1953).
4. I. N. Shkliarevskii, V. K. Miloslavskii: Opt. i Spekt., 3, 361, (1957).
5. I. N. Shkliarevskii, N. G. Starunov, V. G. Padalka: Opt. i Spekt., 4, 792, (1958).
6. J. N. Hodgson: Proc. Phys. Soc., 68B, 593, (1955).
7. K. Forsterling, V. Freedericksz: Ann. d. Phys., 40, 201, (1913).
8. L. R. Ingersoll: Astrophys. J., 32, 265, (1910).
9. M. I. Kaganov, V. V. Slezov, ZETF, 32, 1496, (1957) (See Sov. Phys. JETP).
10. J. R. Beattie, G. K. T. Conn: Phil. Mag., 46, 989, (1955).
11. Handbook of Physical Constants, ONTI, (1937).
12. C. Kittel: Introduction to Solid State Physics, Wiley, N. Y. (1953).

TOM VI, Vyp. 1
TOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar', 1959
January, 1959

On the Theory of Optical Activity in Crystals

I. The Law of Conservation of Energy and the Optical Activity Tensors

F.I. FEDOROV

Abstract. From an assumption concerning the dependence of the induction vectors on the gradients of the corresponding fields, and with the help of the law of conservation of energy, a fundamental relation of Born molecular theory concerning optical activity in crystals is obtained. Through this it is established that the energy flux density vector in optically active media differs from the usual Umov - Poynting vector $c/4\pi\,[\vec{E}\vec{H}]$. Invariant expressions involving symmetry of elements are obtained in a straightforward way for the activity tensors of all classes of optically active crystals.

In the present work a phenomenological theory of optical activity in crystals is based on a principle of invariance derived from the refusal to be restricted to any particular coordinate system.

From the point of view of Maxwell's electromagnetic theory the properties of any medium are characterized by relations among the induction vectors $\vec{D}$, $\vec{B}$ and the fields $\vec{E}$, $\vec{H}$. Considering only linear homogeneous dependence of $\vec{D}$ on $\vec{E}$ and $\vec{B}$ on $\vec{H}$, we arrive at the following relationships:[1]

1) $$D_i = \varepsilon_{ik}E_k + \alpha_{ikl}\nabla_k E_l,$$

2) $$B_i = \mu_{ik}H_k + \beta_{ikl}\nabla_k H_l.$$

These equations represent essentially the only possible generalization of the equations $\vec{D} = \epsilon\vec{E}$, $\vec{B} = \mu\vec{H}$, characterizing inactive crystals, which satisfy the requirement of linearity. The dependence of induction on the gradient of the field is found to be in complete correspondence with the well known fact of molecular theory, that for the description of optical activity it is necessary to take into account phase variations at molecular boundaries.

According to (1) and (2), the parameters characterizing optical activity are represented as the components of two tensors of the third rank, α_{ikl} and β_{ikl}. In the case of non-active crystals, as is well known, the law of conservation of energy imposes a restriction on the property of tensors ϵ and μ, and implies their symmetry. We shall clarify how the restriction imposes this requirement on the nature of tensors α_{ikl} and β_{ikl} which characterize optical activity. In order to obtain the relation expressing the law of conservation of energy, we proceed in the usual way, namely by scalar multiplication of Maxwell's equations.

(3) $$-[\nabla H] + \frac{1}{c}\dot{D} = 0, \quad [\nabla E] + \frac{1}{c}B = 0$$

by $\vec{E}$ and $\vec{H}$ respectively followed by addition. The result is

(4) $$c\,\mathrm{div}\,[EH] + (E\dot{D} + H\dot{B}) = 0.$$

In order for this relation to express the law of conservation of energy it is necessary to put it into the form of the equation of continuity

(5) $$\mathrm{div}\,P + \frac{\partial w}{\partial t} = 0,$$

where $\vec{P}$ is the energy flux density vector and w is the energy density.

Substituting (1), (2) in (4) we obtain

(6) $$c\,\mathrm{div}\,[EH] + E_i(\varepsilon_{ik}\dot{E}_k + \alpha_{ikl}\nabla_k\dot{E}_l) + H_i(\mu_{ik}\dot{H}_k + \beta_{ikl}\nabla_k\dot{H}_l) = 0.$$

As a result of the symmetry of ϵ and μ we have

(7) $$E_i\varepsilon_{ik}\dot{E}_k + H_i\mu_{ik}\dot{H}_k = E\varepsilon\dot{E} + H\mu\dot{H} = \frac{1}{2}\frac{\partial}{\partial t}(E\varepsilon E + H\mu H).$$

Thus, it remains to represent $\alpha_{ikl}\vec{E}_i\nabla_k\vec{E}_l + \beta_{ikl}\vec{H}_i\nabla_k\vec{H}_l$ as a sum of the divergence of a vector and the time derivative of a scalar. First we look at $\alpha_{ikl}\vec{E}_i\nabla_k\vec{E}_l$. We divide this term into equal parts $1/2\,\alpha_{ikl}\vec{E}_i\nabla_k\vec{E}_l$, in one of which we separate out the divergence and in the other the time derivative. We obtain the result

(8) $$\alpha_{ikl}E_i\nabla_k\dot{E}_l = \frac{1}{2}\nabla_k(\alpha_{ikl}E_i\dot{E}_l) - \frac{1}{2}\alpha_{ikl}\dot{E}_l\nabla_k E_i + \frac{1}{2}\frac{\partial}{\partial t}(\alpha_{ikl}E_i\nabla_k E_l) - \frac{1}{2}\alpha_{ikl}\dot{E}_i\nabla_k E_l.$$

Thus, the required form is obtained under the condition:

(9) $$\alpha_{ikl}\dot{E}_l\nabla_k E_i + \alpha_{ikl}\dot{E}_i\nabla_k E_l = \dot{E}_i(\alpha_{ikl} + \alpha_{lki})\nabla_k E_l = 0.$$

Since the last relation must be fulfilled for any field $\vec{E}$, it follows that

(10) $$\alpha_{ikl} + \alpha_{lki} = 0,$$

that is, the tensor α_{ikl} must be anti-symmetric with respect to a permutation of outside indices. Clearly an analogous condition will hold for β_{ikl}. It is possible to represent the tensor α_{ikl} as

(11) $$\alpha_{ikl} = \delta_{inl}\alpha_{nk},$$

where δ_{inl} is the completely antisymmetric unit pseudotensor, and α_{nk} an arbitrary pseudotensor of the second rank. In this case

(12) $$\alpha_{ikl}\nabla_k E_l = \delta_{inl}\alpha_{nk}\nabla_k E_l = \delta_{inl}(\alpha\nabla)_n E_l = [\alpha\nabla, E]_i,$$

in view of which (1) and (2) take the forms

(13) $$D = \varepsilon H + [\alpha\nabla, E],$$

(14) $$B = \mu H + [\beta\nabla, H].$$

Thus, the requirement of conservation of energy leads to an important reduction in the number of independent components of tensors α_{ikl}, β_{ikl}, and for the characteristic connecting relations (1), (2) it appears that tensors α and β of second, not third rank, including 9 parameters rather than 27, are sufficient. We shall call these tensors accordingly the electric and magnetic activity tensors. Relation (4) now takes the form (5), where $w = w_e + w_m$ and

(15) $$w_e = \frac{1}{8\pi}ED = \frac{1}{8\pi}(E\varepsilon E + E[\alpha\nabla, E]),$$

1. It is proposed to sum from 1-3 over the duplicate subscripts.

(16) $$w_m = \frac{1}{8\pi}\mathbf{HB} = \frac{1}{8\pi}(\mathbf{H}\mu\mathbf{H} + \mathbf{H}[\beta\nabla, \mathbf{H}]),$$

(17) $$\mathbf{P} = \frac{c}{4\pi}[\mathbf{EH}] - \frac{1}{8\pi}(\tilde{\alpha}[\mathbf{E}\dot{\mathbf{E}}] + \tilde{\beta}[\mathbf{H}\dot{\mathbf{H}}]);$$

here α, β designate the transposed tensors α, β.

We note, that expressions (15), (16) for the energy densities of electric and magnetic fields preserve the forms $1/8\pi\,\vec{\mathbf{E}}\vec{\mathbf{D}}$ and $1/8\pi\,\vec{\mathbf{H}}\vec{\mathbf{B}}$, where Equations (13), (14) are used for the induction vectors $\vec{D}$ and $\vec{B}$. At the same time it follows from (17), that in media characterized by Equations (1), (2), the electromagnetic energy flux density vector differs from the well known Umov-Poynting vector.[2]

In Sheffer's [1] textbook, the author, starting from Equations (1), (2) and considering that the vector of energy flow must be expressed in the usual way, was able to satisfy the law of conservation of energy only approximately, and even then only by supposing the existence of a definite dependence relation between α and β. By comparing this with our law of energy conservation we see just how tensors α and β exhibit independence.[3]

The whole presentation above relates to an arbitrary electro-magnetic field in media characterized by Equations (1), (2). Let us pass now to the case of plane harmonic electromagnetic waves. In this case all of the field vectors $\vec{E}$, $\vec{H}$, $\vec{D}$, $\vec{B}$ are proportional to the same phase factor $e^{i\varphi}$ where $\varphi = \omega(1/c\ \mathbf{mr} - t)$ and $\vec{m} = n\vec{n}$ is the vector refraction, n the index of refraction, and $\vec{n}$ the wave normal. Substituting the appropriate expressions into Maxwell's Equations (3) and Equations (13), (14) we obtain

(18) $$\mathbf{D} = -[\mathbf{mH}],\ \mathbf{B} = [\mathbf{mE}],$$

(19) $$\mathbf{D} = \varepsilon\mathbf{E} + ik[\alpha\mathbf{m},\ \mathbf{E}],$$

(20) $$\mathbf{B} = \mu\mathbf{H} + ik[\beta\mathbf{m},\ \mathbf{H}],$$

where $k = \omega/c$ wave number. We compare expressions (19) for $\vec{D}$ with the corresponding expression, obtained by Born [4,5] on the basis of the dynamic theory of crystal lattices

(21) $$\mathbf{D} = \varepsilon\mathbf{E} + i[\mathbf{GE}],$$

where $\vec{G}$ is the vector rotation, equal according to Born to

(22) $$\mathbf{G} = g\mathbf{n},$$

and $g = (g_{ik})$ is a tensor, the components of which at a given frequency are taken as constants of the medium. We see that formula (19) coincides with (21), (22) if we stipulate that

(23) $$g = k\alpha.$$

Thus, the fundamental relation (21) of the Born molecular theory of optical activity in crystals may be obtained directly in a phenomenological way from Equation (1) and the law of conservation of energy. The assertion that the parameters g_{ik} appear at a given frequency as constants of matter (see [4], page 555) is inexact, because in a monograph [5] (pages 598, 599, Eq. (170), (178)) it is shown that the vector rotation $\vec{G}$ is proportional to the wave number $\tau = n\,\omega/c$. Consequently the g_{ik} contain the variable index of refraction n, dependent upon the direction of wave propagation in the field corresponding to Eq. (23), and therefore do not appear as constants of matter. If we use the approximation, commonly employed in considering optical activity in crystals [3-5], namely, that of neglecting double refraction in terms where optical activity is small, we may replace n in (23) by a constant mean index of refraction n_0 and then it is possible to take the g_{ik} as constants of matter.

The symmetry of crystals imposes a constraint on tensors α, β. In particular, for certain kinds of crystals α and β must become zero, that is in such crystals optical activity cannot take place. In the present work we show what classes of crystals can possess the active property, and determine expressions for α and β in terms of the symmetry of elements; moreover all results will be derived in invariant form, without recourse to choice of a special coordinate system.

Let S be the matrix of a certain admissible transformation of the symmetry group of a finite crystal. For S an orthogonal matrix, the following relationship is valid

(24) $$S^{-1} = \tilde{S},$$

(25) $$|S| = \pm 1,$$

in which the negative sign applies when transformation S includes reflection. After undergoing a transformation S the vectors $\vec{D}$, $\vec{E}$, V become $\vec{D}' = S\vec{D}$, $\vec{E}' = S\vec{E}$, $V' = SV$.[4] Since the properties of a crystal and its characteristic quantities ϵ, α are not changed by this, Equation (13) remains in force and transformation of the vectors yields

(26) $$S\mathbf{D} = \varepsilon S\mathbf{E} + [\alpha S\nabla,\ S\mathbf{E}].$$

Multiplying by S^{-1}, making use of the usual formula (see [6], Eq. (74))

(27) $$S^{-1}[\mathbf{AB}] = \frac{1}{|S|}[S\mathbf{A},\ S\mathbf{B}],$$

and taking into account (24), (25), we obtain

(28) $$\mathbf{D} = S^{-1}\varepsilon S\mathbf{E} \pm [S^{-1}\alpha S\nabla,\ \mathbf{E}].$$

Comparing with (13), we find finally the conditions imposed upon ϵ and α by the requirement of transformability

(29) $$\varepsilon S = S\varepsilon,$$

(30) $$\alpha S = \pm S\alpha.$$

---

2. We note that Chipart (2), considering the question from another point of view (McCulloch's variational principle, carried over from the elastic theory of light to electrodynamics), also arrived at a vector energy flux density different from $c/4\pi[\vec{E}\vec{H}]$. However, his result differed from our (17).

3. In the book of Landau and Lifschitz relations (10), (13) are obtained by applying the principle of the symmetry of kinetic coefficients. The question concerning the form of the law of conservation of energy under the given conditions, however, is not resolved.

4. We restrict ourselves to study of Eq. (13), since Eq. (14) has a fully analogous form.

Analogously we must have $\mu S = S\mu$, $\beta S = \pm S\beta$. Thus tensors ϵ and μ must commute with matrix S , but tensors α and β must either commute or anticommute with S according to the sign in Eq. (25).

We next investigate in a general way the question of how relations

$$\gamma S = S\gamma \tag{31}$$

$$\gamma S = -S\gamma. \tag{32}$$

impose restrictions on an arbitrary real three-dimensional tensor γ . After multiplying right and left sides by $\tilde{S}$ we find, taking into account (24), that along with (31), (32) the corresponding relations $\tilde{\gamma} = \pm \tilde{S}\gamma$ must hold, so that

$$\gamma(S \pm \tilde{S}) = (S \pm \tilde{S})\gamma, \tag{33}$$

or

$$\gamma(S \pm \tilde{S}) = -(S \pm \tilde{S})\gamma. \tag{34}$$

Transposing Equations (31), (32) and multiplying both sides by S , we obtain $\tilde{\gamma}S = \pm S\tilde{\gamma}$. Consequently, equations (31) - (34) must hold both for γ and for $\tilde{\gamma}$, and also for the half sums and half differences which represent respectively the symmetric and antisymmetric parts of matrix γ .

$$\gamma = \gamma_e + \gamma_a, \quad \gamma_e = \frac{1}{2}(\gamma + \tilde{\gamma}) = \tilde{\gamma}_e, \quad \gamma_a = \frac{1}{2}(\gamma - \tilde{\gamma}) = -\tilde{\gamma}_a = \mathbf{b}^{\times}, \tag{35}$$

where $\vec{b}^{\times}$ is the vector dual of the antisymmetric tensor γ_a [7].

Symmetry transformations of finite crystals may be reduced to the following types (see, e.g. [6,8]).

1. Inverting

$$C = -1. \tag{36}$$

2. Plane symmetric (reflection in a plane, perpendicular to unit vector $\vec{e}$)

$$P = 1 - 2e \cdot e. \tag{37}$$

3. Axially symmetric (rotation through an angle $\varphi_k = 2\pi/k$, $k = 2,3,4,6$ about unit vector $\vec{e}$)

$$L_k = e \cdot e + \cos\varphi_k (1 - e \cdot e) + \sin\varphi_k e^{\times}. \tag{38}$$

4. Axial inverting (combined rotation (38) and inversion (36))

$$L_{ik} = CL_k = L_k C = -L_k, \quad k = 4, 6 \tag{39}$$

and their combinations.[5]

We investigate next what restrictions are imposed on γ by condition (31). It is evident that the condition $\gamma C = C\gamma$ is always satisfied. Condition $\gamma P = P\gamma$ gives

$$\gamma e \cdot e = e \cdot e\gamma. \tag{40}$$

By multiplying the left and right sides by $\vec{e}$ we obtain

$$\gamma e = e\gamma = \tilde{\gamma} e = e\gamma e \cdot e = ae, \tag{41}$$

where $a = \vec{e}\gamma\vec{e}$ is a number. Thus, if $\gamma P = P\gamma$, then vector $\vec{e}$ appears as an eigenvector of matrix γ or $\tilde{\gamma}$.

Equations (33) with $S = L_k$ (38) yield (40) and

$$\sin\varphi_k (\gamma e^{\times} - e^{\times}\gamma) = 0. \tag{42}$$

Here two cases can occur. If $\sin\varphi_k = \sin 2\pi/k = 0$, the first occurs for $k = 2$ (second order axis of symmetry). In this condition $\gamma L_2 = L_2\gamma$ reduces to (40), i.e., the direction of the second order axis $\vec{e}$ gives the eigen vector of matrix γ or $\tilde{\gamma}$. If, on the other hand, $k = 3, 4, 6$, i.e., a higher order axis of symmetry is present, then along with (40) we obtain the condition

$$\gamma e^{\times} - e^{\times}\gamma = 0. \tag{43}$$

According to the above, (40) and (43) must hold for $\gamma_c = 1/2(\gamma + \tilde{\gamma})$ and $\gamma_a = \vec{b}^{\times}$. One is easily convinced, that from $\vec{b}^{\times}\vec{e}^{\times} - \vec{e}^{\times}\vec{b}^{\times} = \vec{e}\cdot\vec{b} - \vec{b}\cdot\vec{e}$ it follows that $\vec{b}$ is parallel to $\vec{e}$, or $\vec{b} = c\vec{e}$. Thus, $\gamma_a = c\vec{e}^{\times}$. In its turn, the symmetrical part can always be represented in the following way (see [6])

$$\gamma_e = ae \cdot e + a'e' \cdot e' + a''e'' \cdot e'', \tag{44}$$

where a, a', a'' are eigen values, $\vec{e}$, $\vec{e}'$, $\vec{e}''$ the corresponding mutually orthogonal unit eigenvectors of matrix γ_c . Substituting (44) into (43), and taking into account, that $[\vec{e}\vec{e}'] = \vec{e}''$, $[\vec{e}\vec{e}''] = -\vec{e}'$, we obtain

$$-a'e' \cdot e'' + a''e'' \cdot e' = a'e'' \cdot e' - a''e' \cdot e'', \tag{45}$$

from which it follows that $a' = a''$. In this case (see [9]) $\gamma_c = a' + (a - a')\vec{e}\cdot\vec{e}$. So, for the existence of symmetry axes of higher than second order, condition $\gamma L_k = L_k\gamma$ leads to the following general expression for γ

$$\gamma = \gamma_e + \gamma_a = a + be \cdot e + ce^{\times}, \tag{46}$$

where $\vec{e}$ is the unit vector along the symmetry axis. With this (40) is satisfied identically. With $S = L_{ik}$ condition (31) does not give anything new.

Let us now examine the anti-commutativity condition (32). According to the above, here the transformation S may be either an inversion C , reflection in a plane P , or an axial inversion $L_{ik} = -L_k$. If, $S = \tilde{S} = -1$, then, from (32) it follows that $\gamma = -\gamma = 0$. Thus, crystals with inversion symmetry cannot be optically active. Condition (32) with $S = P$ takes the form

$$\gamma = \gamma e \cdot e + e \cdot e\gamma. \tag{47}$$

For $\gamma_a = \vec{b}^{\times}$ it follows from this that $\vec{b}^{\times} = [\vec{b}\vec{e}]\cdot\vec{e} + \vec{e}\cdot[\vec{e}\vec{b}]$ which after multiplication by $\vec{b}$ gives $\vec{b}\vec{e} = 0$. For γ_c we have from (47) the indication $\gamma_c e = e\gamma_c = a$: $\gamma_c = a\cdot e + e\cdot a$. With this, multiplication of (47) by $\vec{e}$ gives $\vec{e}\gamma\vec{e} = \vec{e}\gamma_c\vec{e} = 2a\vec{e} = 0$. Thus, condition (32) with $S = P$ gives finally

$$\gamma = a \cdot e + e \cdot a + b^{\times}, \quad ae = be = 0, \tag{48}$$

where $\vec{e}$ is normal to the plane of symmetry. It is easy to prove, that (48) satisfies (47).

With $S = L_{ik} = -L_k$ condition (34) takes the form

$$2\cos\varphi_k\gamma + (1 - \cos\varphi_k)(\gamma e \cdot e + e \cdot e\gamma) = 0, \tag{49}$$

$$\gamma e^{\times} + e^{\times}\gamma = 0. \tag{50}$$

For $\gamma_a = \vec{b}^{\times}$ from (50) we have $\vec{b}^{\times}\vec{e}^{\times} + \vec{e}^{\times}\vec{b}^{\times} = \vec{e}\cdot\vec{b} + \vec{b}\cdot\vec{e} - 2\vec{b}e = 0$. Because the sum of the two dyads $\vec{e}\cdot\vec{b} + \vec{b}\cdot\vec{e}$ cannot be proportional to a unit tensor, then $\vec{b} = 0$. This means, $\gamma = \tilde{\gamma} = \gamma_c$. From (50) it follows that $\gamma\vec{e}^{\times 2} = \vec{e}^{\times 2}\gamma = \gamma(\vec{e}\cdot\vec{e} - 1) = (\vec{e}\cdot\vec{e} - 1)\gamma$, therefore $\gamma\vec{e}\cdot\vec{e} + \vec{e}\cdot\vec{e}\gamma = 2(\gamma + \gamma\vec{e}^{\times 2})$ in view of which (49) takes the form

$$\gamma + (1 - \cos\varphi_k)\gamma e^{\times 2} = 0. \tag{51}$$

5. Expression $\vec{e}\cdot\vec{e}$ denotes a dyad, $\vec{e}^{\times}$ the tensor dual of vector e [7], defined by the condition $\vec{e}^{\times}\vec{A} = -\vec{A}\vec{e}^{\times} = [\vec{e}\vec{A}]$, where $\vec{A}$ is an arbitrary vector ($\vec{e}^{\times} = -\vec{e}^{\times}$) .

After multiplying by $\vec{e}$ it follows from this that $\gamma e = 0$. But in this case $\gamma e^{x2} = -\gamma$ and (51) reduces to $\cos \varphi_k \gamma = 0$. This means, that $\gamma \neq 0$ only for $\varphi_k = \pi/2$ or $k = 4$. Thus, in the presence of an inversion axis optical activity is possible only if the order of the axis is equal to four. Since $\gamma\vec{e} = 0$, tensor γ must consist of two dyads (see [6]). Most conveniently it can be written in the form

$$\gamma = \vec{a}\cdot\vec{e}_o + \vec{a}^* \cdot \vec{e}^*_o , \tag{52}$$

where $\vec{ae} = \vec{a}^*\vec{e} = 0$, e_o is the "rotation" vector [10], defined by the following conditions: $[\vec{ee}_o] = i\vec{e}_o$, $[\vec{ee}^*_o] = -i\vec{e}^*_o$, $\vec{ee}^*_o = |\vec{e}_o|^2 = 1$. From (50) it follows that $\gamma e^{*2} = -\gamma = -e^x\gamma e^x$; substituting here (52), we obtain by taking into account the properties of $\vec{e}_o$.

$$\gamma = \vec{a}\cdot\vec{e}_o + \vec{a}^*\cdot\vec{e}^*_o = e^x\gamma e^x = [\vec{ea}]\cdot - i\vec{e}_o + [\vec{ea}^*]\cdot i\vec{e}^*_o$$

Hence, $[\vec{ea}] = i\vec{a}$, $[\vec{ea}^*] = -i\vec{a}^*$, i.e., $\vec{a}$ is a rotation vector, proportional to $\vec{e}_o$: $\vec{a} = c\vec{e}_o$. Thus

$$\gamma = c\vec{e}_o\cdot\vec{e}_o + c^*\vec{e}^*_o\cdot\vec{e}^*_o . \tag{53}$$

Let us now consider a combination of various cases, characteristic of different classes of crystals. If there are two mutually perpendicular axes of symmetry of order higher than two, $\vec{e}'$ and $\vec{e}''$, then, according to (46), we must have simultaneously

$$\gamma = a + b\vec{e}\cdot\vec{e} + c\vec{e}^x = a' + b'\vec{e}'\cdot\vec{e}' + c'\vec{e}'^x .$$

Comparison of the antisymmetrical terms gives $c = c' = 0$. After this, multiplying by e, e', we obtain $b = b' = 0$, $a = a'$. Thus, the presence of two mutually perpendicular axes of symmetry of order higher than two implies $\gamma = a$, i.e., the scalar character of tensor γ. This property is incompatible with the existence in the planar class, of cubic syngony of the symmetry planes because here $\gamma P + P\gamma = 2aP = 0$, i.e., $a = \gamma = 0$.

For planar classes of central syngony, thanks to the presence of planes of symmetry parallel to the axis of symmetry $\vec{e}$ (see [8]) Equations (46) and (48) must hold simultaneously, i.e.

$$\gamma = a + b\vec{e}\cdot\vec{e} + c\vec{e}^x = a\cdot\vec{e}'\vec{e}' + \vec{e}'\cdot\vec{a}\vec{e}'^x, \quad \vec{ae}' = \vec{be}' = \vec{ee}' = 0.$$

Comparing the symmetric and antisymmetric parts, we obtain at once $b = c\vec{e}$, $\vec{a}\cdot\vec{e}' + \vec{e}'\cdot\vec{a} = a + b\vec{e}\cdot\vec{e}$. From the last equation, multiplying by $\vec{e}'$, we arrive at $a = \vec{ae} = 0$. Consequently, for planar classes of central symmetry the activity tensors may be different from zero and take the form

$$\alpha = c\vec{e}^x , \quad \beta = c'\vec{e}^{*x} , \tag{54}$$

where $\vec{e}$ is a unit vector along the axis of symmetry.

For planar classes of rhombic symmetry we must have (see (41), (48))

$$\gamma\vec{e} = \vec{e}\gamma = a\vec{e}, \quad \gamma = \vec{a}\cdot\vec{e}'\vec{e}' + \vec{e}'\cdot\vec{a} + b^x, \quad \vec{e}'\vec{a} = \vec{e}'\vec{b} = \vec{e}'\vec{e} = 0 .$$

Multiplying by e on the right and on the left, we obtain $\vec{ea}\cdot\vec{e}' + [\vec{ep}] = \vec{e}'\cdot\vec{ae} + [\vec{pe}] = a\vec{e}$, from which $[\vec{be}] = 0$, $b = ce$, $a = ae = 0$, $\vec{a} = b[\vec{ee}'] = b\vec{e}''$, where $\vec{e}''$ is a vector normal to the second plane of symmetry. Hence, for the planar class of rhombic symmetry

$$\gamma = b(\vec{e}'\cdot\vec{e}'' + \vec{e}''\cdot\vec{e}') + c\vec{e}^x , \tag{55}$$

where $\vec{e}$ is a vector along the axis of symmetry, $\vec{e}'$, $\vec{e}''$ normals to the planes of symmetry. The presence, in axial classes of central symmetry of second order axes $\vec{e}'$ perpendicular to higher order axes $\vec{e}$ leads to the relations (see (41), (46))

$$\gamma = a + b\vec{e}\cdot\vec{e} = c\vec{e}^x, \quad \gamma\vec{e}' = \vec{e}'\gamma = a'\vec{e}', \quad \vec{ee}' = 0 .$$

Thus, for axial classes of central symmetry

$$\gamma = a + b\vec{e}\cdot\vec{e} ,$$

where e is the symmetry axis of higher order. In the case of an axial class of rhombic symmetry the existence of three mutually perpendicular axes of the second order implies

$$\vec{e}_i\gamma = \gamma\vec{e}_i = a_i\vec{e}_i, \quad \vec{e}_i\vec{e}_k = \delta_{ik} ,$$

where $\vec{e}_i$ are vectors of axes L_2. Because tensor γ gives identical results when multiplied left and right by three independent vectors, it is symmetrical and may be expressed in the form (see [6])

$$\gamma = a_1\vec{e}_1\cdot\vec{e}_1 + a_2\vec{e}_2\cdot\vec{e}_2 + a_3\vec{e}_3\cdot\vec{e}_3 . \tag{57}$$

Finally, in the inversion-planar class with tetragonal symmetry, for an inversion axis of the 4th order, $L_i4 \| e$ is added perpendicularly to its axis of symmetry $L_2 \| \vec{e}'$. Since e' lies in the plane of $\vec{e}_o$, $\vec{e}^*_o$ (see (53)) we have

$$\vec{e}_o = \frac{1}{2}(\vec{e}' + i\vec{e}''), \quad \vec{e}^*_o = \frac{1}{2}(\vec{e}' - i\vec{e}''), \quad \vec{e}'\vec{e}'' = 0, \quad \vec{e}'^2 = \vec{e}''^2 = 1 , \tag{58}$$

where $\vec{e}''$ is the vector of the second axis L_2. Because, according to (41) $\gamma\vec{e}' = a\vec{e}'$ and $\vec{e}_o\vec{e}' = \vec{e}^*_o\vec{e}' = 1/2$, then utilizing (53), we obtain $\gamma\vec{e}' = 1/2(c\vec{e}_o + c^*\vec{e}^*_o) = a\vec{e}'$. Multiplying this equation by $\vec{e}_o$ and $\vec{e}^*_o$, we obtain $c = c^*$. Thus for inversion-planar class Equation (53) is simplified and takes the form $\gamma = c(\vec{e}_o\cdot\vec{e}_o + \vec{e}^*_o\cdot\vec{e}^*_o)$, or using (58)

$$\gamma = c(\vec{e}'\cdot\vec{e}' - \vec{e}''\cdot\vec{e}''), \quad \vec{e}'\vec{e}'' = 0 , \tag{59}$$

where $\vec{e}'$, $\vec{e}''$ is a unit vector along axis L_2, perpendicular to L_i4.[6]

Thus, in 32 classes of crystals the activity tensors become zero for all central and planaxial classes (11 in number), possessing inverted symmetry. Eliminated also are both inversion classes of hexagonal symmetry (having an inverted axis of the 6th order) and planar classes of cubic symmetry. The remaining 18 classes of crystal symmetry may possess the property of optical activity.

6. It is not difficult to convince oneself, that with the help of unit vectors e_1, e_2 normal to the planes of symmetry for given angles between the two halves of the axes of the second order, tensor (59) may take the form

$$\gamma = c(\vec{e}_1\cdot\vec{e}_2 + \vec{e}_2\cdot\vec{e}_1), \quad \vec{e}_1\vec{e}_2 = \vec{e}_1\vec{e} = \vec{e}_2\vec{e} = 0 .$$

References

K. Scheffer: Theoretical Physics, 3,2. Optika. GONTI, 1938.

H. Chipart: Comptes rendus, 178, 77, 995, 1532, 1805, 1967, (1924.)

L. D. Landau and E. M. Lifschitz: Electrodynamics of Continuous Media, GITTL, 1957.

M. Born: Optics. GNTIY, 1937.

M. Born: Atomtheorie des festen Zustandes, Leipzig, 1923.

6. N. E. Kochin: Vector analysis and elements of tensor analysis, Publ. A. N. USSR, 1951.
7. F. I. Fedorov: Opt. i Spektr., 1, 926(1956).
8. G. M. Popov and I. I. Shafranovski: Crystallography. GNTI, 1955.
9. F. I. Fedorov: TR. Inst. of Phys. and Math. AN BSSR 2, 230(1957).
10. F. I. Fedorov: DAN USSR 102, 69(1956).

TOM VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar', 1959
VOL. VI, No. 1 OPTICS AND SPECTROSCOPY January, 1959

BRIEF REPORTS

Interference Mirror on an Aluminum Substrate

K.I. TARASOV

The coefficients of reflection R, transmission T and absorption A, of the mirror of a Fabry-Perot interferometer determine completely the spectral picture of this instrument: R its resolving power, and A/T the intensity of the interference rings.

We are presented with the problem of producing a mirror with the least possible ratio A/T for high enough R in the 3200 - 5600 Å range.

Multilayer dielectric mirrors [1-6] have high enough R in the comparatively narrow band of the spectrum 700 - 800 Å, consequently, we should deposit films of the dielectrics SiO_2 and TiO_2 on an aluminum substrate in order to broaden the working section of the spectrum. The invariance of the ratio A/T when non-absorbing films are deposited on a metal affords the possibility of using a thin aluminum layer with a reduced value of A/T, and even with a low R, as the substrate and then of raising R to the value we require, while retaining the ratio A/T unchanged, by depositing several films of SiO_2 and TiO_2.

In order to compute the thickness and the total number of dielectric films which must be deposited on the aluminum, it is necessary to know the phase shift on reflection of the light from the aluminum into the dielectric; the magnitude of R at the metal-dielectric interface, which cannot be measured directly, depends on the magnitude of this shift also.

The magnitude of the phase shift was determined experimentally as follows. Very thin dielectric layers of as identical thickness as possible were superposed on a metal mirror, where the reflection coefficient was measured each time. This coefficient is a periodic function of the total thickness of the films deposited. It first decreases, where the first minimum occurs if and only if the phase difference φ of the rays reflected from both faces of the dielectric is 2π along with the phase shift δ, the first maximum occurs at 3π. Hence, knowing the thickness of the dielectric at which R takes on the extremum values, the phase shift can be determined for the reflection from a metal into a dielectric. The data we obtained are presented in tables 1 and 2.

Table 1. Phase shift δ in fractions of π for reflection at an angle of 3.5° from aluminum into silicon dioxide.

λ (in Å)	δ
4060	1.17 ± 0.05
4300	1.13 ± 0.11
5400	1.16 ± 0.07
6900	1.09 ± 0.08

The selection of a dielectric film thickness for a two-layer covering is of no special difficulty. Graphs of R as a function of the thickness of a silicon dioxide layer (from which the first film was deposited in this case) were constructed from several wavelengths. It is expedient to select the first interface of the media where a reflection minimum occurs for the majority of wavelengths since the phase shift when a TiO_2 is deposited on the SiO_2 will become zero and the reflection minimum will be replaced by a maximum. The second boundary corresponds to that thickness of TiO_2 at which the reflection coefficient of the average wavelength of the selected spectral region achieves a maximum.

Table 2. Phase shift δ in fractions of π for reflection at an angle of 29° from aluminum into silicon dioxide.

λ (in Å)	δ
3200	1.41 ± 0.03
3600	1.21 ± 0.05
4000	1.11 ∓ 0.04
4800	1.06 ± 0.07
5600	1.04 ± 0.06
6400	1.08 ± 0.10

In analyzing a large even number of films, it is necessary to keep in mind that the amplitude reflection coefficient of the air-TiO_2 interface is almost twice the reflection coefficient of the TiO_2-SiO_2 interface, and that the reduction in the reflection from the metal surface when the dielectric SiO_2 is deposited is approximately equal to the reflection from the TiO_2-SiO_2 interface. Consequently, a minimum reflection coefficient certainly exists in the case of four dielectric films on a metal, which will approximately equal the reflection coefficient of the air-metal interface. This holds for that wavelength at which a ray reflected from the TiO_2-SiO_2 interface is opposite in phase to a ray reflected from the metal. Hence, four films on aluminum yield worse results than do two films. Computation shows that the deposition of six or eight films yields a somewhat better result than the deposition of two films, however, in practice this improvement is hard to realize because of the inaccurate control of the film thickness during deposition and because of the growth of the absorption in TiO_2 in the shortwave band.

In the case of an odd number of films on a metal, where the first film is TiO_2, the first reflection extremum is a minimum, as before; however, it is impossible here to select the interface since the minimum does not transform into a maximum when SiO_2 is deposited on the TiO_2. Hence, we cannot use this most suitable (in the achromatic sense) extremum. In addition, the reflection coefficient from the aluminum into the TiO_2 is lower than in the SiO_2 and the diminution in the reflection from the metal when the dielectric TiO_2 replaces the air is compensated by two TiO_2-SiO_2 interfaces rather than one. Thus, the case of an odd number of films, which is more difficult for the achromatization of a mirror than is the even number of films, has no advantages in the production of a higher reflection coefficient.

The spectral width of the reflection maximum of the interference mirror can be taken as that spectral region at whose boundaries the mirror re-

lection coefficient R equals the reflection oefficient of the metallic substrate in air R_M ; ne reflection coefficient drops off rapidly outside the limits of this section.

The computation and the experiment conducted now that if 3300-3400 Å (the range where the osorption in the TiO_2 is still small for our ilms) is taken as the lower boundary, then the pper boundary will be 5600 Å in the case of two ilms, where the increment in the reflection coefficients achieves its maximum at 4200 Å , somewhat ess (by 1-2%) than the value $\frac{1}{2}(1 - R_M)$. Here, he ratio A/T is unchanged in practice.

Presented in Table 3 are the reflection coefficients of certain mirrors for different wavelengths.

We will not present here the values of the ransmission coefficient because the ratio of the bsorption and transmission coefficients for all he mirrors produced did not change before and fter depositing the films on the metal. A small ncrease in this ratio occurs just at $\lambda = 3200$ Å .

It should be noted that the deposition of SiO_2 and TiO_2 films on aluminum raises its mechanical strength significantly; such a mirror can e rubbed with cotton wetted with alcohol, without ear of scratching its surface.

January 13, 1958

References

1. G. V. Rozenberg: Usp. Fiz. Nauk, 47, 3, 1952.
2. P. G. Kard: DAN USSR, 108, 60, 1956.
3. P. W. Baumeister, J. M. Stone: J. Opt. Soc. 46, 228, 1956.
4. W. L. Barr, F. A. Jenkins: J. Opt. Soc. Amer., 46, 141, 1957.
5. R. D. MATTUCK: J. Opt. Soc. Amer., 46, 621, 1957.
6. D. S. Smith: J. Opt. Soc. Amer., 48, 43, 1958.

Table 3. Rise in the reflection coefficient of an aluminum mirror with the deposition of two dielectric films (SiO_2 and TiO_2) .

mirror number	Substrate	λ (в Å)								
		3200	3600	4000	4400	4800	5200	5600	6000	6400
1	Al	82.5	84.7	86.0	86.1	86.1	86.5	86.2	85.1	84.0
	Al + SiO_2 + TiO_2	78.8	91.2	92.5	91.8	91.0	88.0	85.3	81.9	79.0
2	Al	77.5	80.5	82.0	83.6	83.9	84.0	84.0	83.0	82.2
	Al + SiO_2 + TiO_2	79.5	89.5	89.0	87.1	85.0	81.5	78.0	74.0	70.6
3	Al	67.7	71.6	74.3	75.8	76.2	76.5	77.2	77.2	77.0
	Al + SiO_2 + TiO_2	ок. 45	73.2	82.8	85.0	84.5	83.0	81.5	79.0	76.5
4	Al	65.0	69.0	72.5	74.8	76.0	76.6	77.0	77.4	77.4
	Al + SiO_2 + TiO_2	53.5	76.8	80.3	79.3	78.0	77.0	73.4	70.0	66.5
5	Al	66.0	70.7	74.0	76.3	77.0	77.7	78.5	79.0	79.0
	Al + SiO_2 + TiO_2	39.5	75.0	81.5	82.5	82.0	80.8	77.0	74.5	70.8

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

Determination of the Temperature of a Vacuum Spark

E. A. AKIMOV, I. P. MALKOV

The objective of our work was the determination of the temperature of a vacuum spark by relative intensity of the lines in the Al III spectrum. It was assumed that the Boltzmann distribution of the particles by energy levels is correct. Then the intensity of the spectral line in an absence of reabsorption is related to the temperature by

$$I_i = \frac{g_i}{g_o} h\nu_i A_i N_o e^{-\frac{E_i}{kT}}$$

where N_o is the density of the radiating atoms, E_i - excitation energy of a given level, ν_i - radiation frequency of a given line, I_i - intensity of the spectral line, g_i and g_o - statistical weights in excited and unexcited states, A_i - probability of a transition.

Measuring the relative intensity of the lines with certain values of the probability of a transition A_i , one may determine the temperature of a light source.

This method is applicable to stationary processes only. Non-stationary processes, taking place in a vacuum spark, are related to the starting of the electric breakdown of the vacuum gap, and following the spark discharge, an equilibrium in the form of an arc, is reached [1]. The time required to establish the state of equilibrium, for the case of a spark, occurring at atmospheric pressure, is on the order of 10^{-7} sec. [2]. In vacuum, the equilibrium is established faster [3]. The impulse duration, also depending on the network parameters, is at least one order of magnitude of time larger than the time required to establish the equilibrium condition.

It is well established, both theoretically and experimentally, that the particle distribution by energy levels in the channel of a spark burning at atmospheric pressure, is described by Boltzmann's equation in the state of equilibrium, with decided importance attached to the value of the free electron density. The density of $N = 10^{17}$, occurring in an atmospheric spark, is already sufficient to produce a Boltzmann distribution [2]. Since the discharge networks (large capacitors and small inductances) and the considerable breakdown voltages used in the case of a vacuum spark produce large current densities, it may be supposed that the electron concentration in a vacuum spark is sufficiently large, and not smaller than the one in an atmospheric spark. Thus, it may be assumed that for a vacuum spark there is a Boltzmann distribution of particles.

The circuit of a spark is shown in the Figure. The discharge network contains a capacitor which is being charged through a limiting resistor by a rectifier. As soon as the capacitor voltage reaches a sufficiently high value, breakdown occurs.

The inductance of the discharge network amounted to about 6 microhenries and consisted of the inductance of the leads. Aluminum electrodes were used; the electrode separation was about 0.5 mm . Breakdown voltage was on the average 35-40 kv . In order to eliminate frequency breakdowns to the frame, a glass frame was used in the construction of the source.

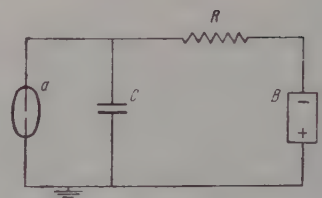


Figure. Electrical Diagram of the Spark. R = 4 megohm, C = 0.27 μf , a - spark gap , B - rectifier.

The spectra were obtained by using a DFS-6 vacuum spectrograph with a grazing incidence concave diffraction grating. The working vacuum in the spectrograph and in the source was 10^{-3} mm Hg . Principal lines of the main and diffuse series of the Al III spectrum were used for the determination of temperature; the other members of the series were absent from the spectrogram because of low intensity. The wavelengths of these lines and the corresponding transitions are: 1862.90 Å ($3S_{1/2}$ - $3P_{1/2}$) and 1605.7 Å ($3P_{1/2}$ - $3D_{3/2}$) , 1854.7 Å ($3S_{1/2}$ - $3P_{3/2}$) and 1605.7 Å ($3P_{1/2}$ - $3D_{3/2}$) .

The calculation of the probabilities of transitions for the lines of simple atomic systems, like Al III, is simplified by the fact that a method described in [4] may be used, whereby matrix elements of the dipole moments may be evaluated using a Coulomb potential approximation. This method gives results for simple atomic systems which agree closely with experimental data. The matrix elements of dipole moments are tabulated in the mentioned reference and their determination presents no difficulty. The ratio of probabilities of transitions was calculated by us by means of the formula:

$$\frac{A_1}{A_2} = \frac{\max(l_1, l_1')(E_1^{nl} - E_1^{n'l'})^3 (r_1^{ij})^2 (2l_2 + 1)}{\max(l_2, l_2')(E_2^{nl} - E_2^{n'l'})^3 (r_2^{ij})^2 (2l_1 + 1)} ,$$

where l and l' are orbital quantum numbers for lower and upper levels, E^{nl} and $E^{n'l'}$ are the values of energy, corresponding to initial and final levels, $r_{ij} = \int_0^\infty f_i(r) r f_j(r) dr$ - the matrix element (of the function $f_k(r)$ - the radial parts of the wave functions of the valence electron). The lower index in this notation indicates the relationship to the spectral line. The values of the corresponding energy levels were taken from Tables [

The ratio of the intensities of separate components of the resonance doublet is close to the theoretical one (0.55 while the theoretical is 0.5), which indicates low reabsorption and makes it possible to determine the temperature by the described relative - intensity - of - the - lines metho

The method of luminescent photometry was used to convert from blackening to intensities.* Films

* Editor's note: From what follows in the remainder of the article, it is clear that the author mean to convey the fact that luminescent photometry was used to change spectrum line radiation into plate blackening. SPD

DN type with an exposure index of 250 units GOST** , sensitized by an alcohol solution of sodium salicylate, were used as the photographic material. Taking into account the constancy of the quantum efficiency for sodium salicylate and the independence of its luminescence spectrum from the wavelength of the exciting light in the broad vacuum ultraviolet region, the ratio of intensities of incident light for two different wavelengths is expressed by a ratio of intensities, measured with respect to the blackening:

$$\frac{I_{\lambda_1}}{I_{\lambda_2}} = \frac{I_{l\lambda_1}}{I_{l\lambda_2}} \cdot \frac{\lambda_2}{\lambda_1},$$

where λ is the wavelength, I_λ - intensity of incident light, $I_{l\lambda}$ - intensity of luminescence (intensity measured by degree of blackening). The blackened areas were marked using a step reducer on a non-sensitized film at the 3850 Å wavelength, which is the center of the sodium salicylate luminescence spectrum [6].

The formula for the determination of the temperature has the form

$$T = \frac{E_1 - E_2}{k \ln \frac{I_{l\lambda_2} g_1 A_1}{I_{l\lambda_1} g_2 A_2}}.$$

The values of temperature turn out to be equal to 45000° K (the lines 1862.9 and 1605.7 Å) and to 47000° K (the lines 1854.67 and 1605.7 Å).

These results must be interpreted as the temperatures of the Al III ions at the instant of excitation. Due to the oscillating nature of the discharge (because of voltage fluctuations at the electrodes during the impulse) it is difficult to say whether these are maximum temperatures or not.

The conditions of the experiment are such that, since the whole volume of the spark channel participates in the formation of spectral lines, the results indicate some average volume temperature.

The obtained values of temperature contain errors associated with the calculation of the probability of transitions as well as errors due to photometric measurements, and it is not clear how these errors may be evaluated.

The error of the result may be found only by comparing the results of measurements made by using various lines, and the measurement of temperature using various radiators; agreement of the results would experimentally confirm the existence of a definite temperature in the spark channel. Therefore, it is desirable that the temperature be measured by spectral lines of other elements.

In conclusion, the author expresses gratitude to A. R. Striganov for the discussions and the interest in this work.

** GOST are the initials for the Government Standards Office.

References

1. N. B. Rozanova, V. L. Granovskii: ZTF, 26, 489, (1956)
2. S. L. Mandel'shtam, N. K. Sukhodrev: ZETF, 24, 701 (1953)
3. J. K. Boyce: UFN, 30, 245 (1946)
4. B. Bates: Phil. Trans. Roy. Soc. A242, 101 (1950)
5. C. Moore: Atomic Energy Levels, vol. I, Washington, 1949
6. H. Creiner: Z. Naturforschg., 12a, 735 (1957)

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar', 1959
January, 1959

Influence of Impurity Concentration on the Quantum Efficiency of Luminescence as a Function of Anthracene Crystal Thickness

A. N. FAIDYSH, V. L. ZIMA

It has been shown in [2] that the ratio of the quantum efficiencies of the luminescence of anthracene (B_a) to that of the impurity, naphthacene, (B_n) increases as the thickness of the anthracene crystals diminishes. The influence of the concentration of the impurity, naphthacene, in anthracene crystals on the effect mentioned has been investigated herein.

The naphthacene concentration had the following values in the samples being investigated: $3\cdot10^{-6}$; $8\cdot10^{-6}$; $3\cdot10^{-5}$ and $1\cdot10^{-4}$ mole/mole. The luminescence quantum efficiencies were measured on a photoelectric apparatus and by the method of photographic heterochromatic photometry.

The results obtained are presented on figures 1 - 4. Shown on figure 1 is the luminescence quantum efficiency of anthracene as a function of the film thickness for four naphthacene concentrations. It is seen from figure 1 that the quantum efficiency of anthracene increases by approximately 10% for the transition from thick films to thin ($d \approx 1\mu$) for a naphthacene concentration on the order of 10^{-6} mole/mole and increases by 40% for a concentration of 10^{-4} mole/mole.

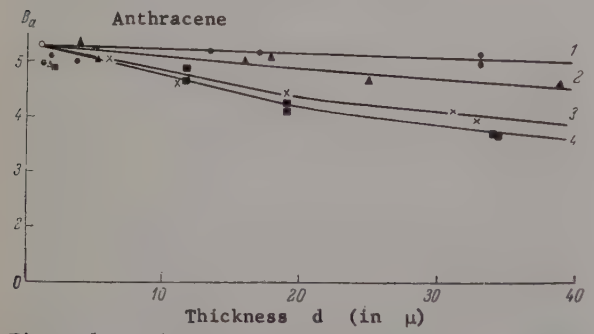


Figure 1. Relative quantum efficiency of anthracene luminescence (B_a) as a function of film thickness. Concentration in mole/mole : $1\text{-}3\cdot10^{-6}$; $2\text{-}8\cdot10^{-6}$; $3\text{-}3\cdot10^{-5}$; $4\text{-}1\cdot10^{-4}$.

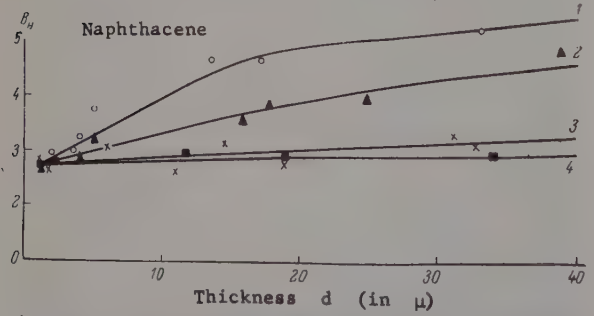


Figure 2. Relative quantum efficiency of naphthacene luminescence (B_n) as a function of film thickness. Concentration in mole/mole: $1\text{-}3\cdot10^{-6}$; $2\text{-}8\cdot10^{-6}$; $3\text{-}3\cdot10^{-5}$; $4\text{-}1\cdot10^{-4}$.

The luminescence quantum efficiency of naphthacene is shown on figure 2 as a function of film thickness. In this case a decrease in the thickness from 40 to 1μ is accompanied by a significant change in B_n (80 - 90%) for low naphthacene concentrations ($3\cdot10^{-6}$ mole/mole) and a small change (approximately 10%) for high concentration (10^{-4} mole/mole).

Presented on figure 3 is the ratio B_n/B_a as a function of the film thickness (for a thickness $d = 0.2\mu$ the values of B_n/B_a are equal for various concentrations). As is seen from the curves, the change in B_n/B_a also depends on the impurity concentration as the thickness of the thin films decreases ($d < 1\mu$). This ratio decreases approximately 2.5 times for a high naphthacene concentration (10^{-4} mole/mole) for the change from 1 to 0.2μ and decreases 3.2 times for a low concentration ($3\cdot10^{-6}$ mole/mole). It should be noted that ratio B_n/B_a changes very radically approximately as the film thickness decreases below 0.3μ. Thus, for example, a change from 1 to 0.2μ leads to a 2.5 times decrease in B_n/B_a and a change from 1 to 0.15μ to a 3.3 times decrease for a 10^{-4} mole/mole concentration.

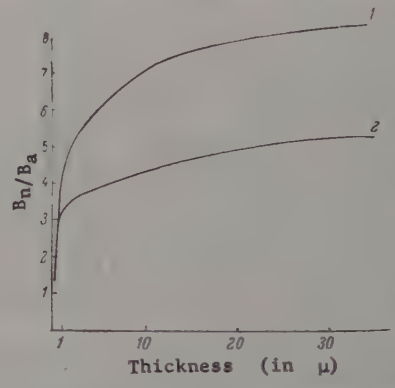


Figure 3. The ratio B_n/B_a as a function of film thickness. Concentration in mole/mole: $1\text{-}3\cdot10^{-6}$; $2\text{-}1\cdot10^{-4}$.

The measurements made for a 10^{-4} mole/mole naphthacene concentration showed that an increase in the crystal thickness from 30 - 40μ to tenths of a millimeter leads to an increase in B_n/B_a of approximately 20%.

The energy distribution in the luminescence spectrum of anthracene with an impurity of $3\cdot10^{-5}$ mole/mole naphthacene is presented on figure 4 for film thicknesses of 40 and 0.2μ.

In agreement with photoelectric measurements, it is seen from figure 4 that the transition from thick to thin films leads to a significant decrease in the quantum efficiency of naphthacene and to an increase in the quantum efficiency of anthracene. The quantum efficiency of the naphthacene is proportional to the area under the $I/h\nu$ curve in the 20,600 - 16,500 cm^{-1} spectrum range and the quantum efficiency of anthracene in the 25,000 - 20,600 cm^{-1} band. A significant redistribution of the energy occurs in the transition from a thick to thin film because of reabsorption in the anthracene spectrum. There are no significant changes in the luminescence spectrum of naphthacene.

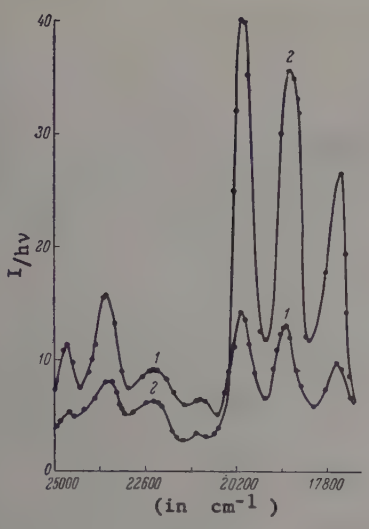


Figure 4. Energy distribution in the luminescence spectrum of impurity anthracene crystals. Thickness d : 1 - 0.2μ; 2 - 40μ.

The established dependence of the quantum efficiency on the crystal thickness and the impurity concentration can be explained as follows. There are two reasons for the dependence of B_a/B_n on the crystal thickness. In thin enough films (d < 1μ), a decrease in the crystal thickness leads to an increase in the number of excitons incident on the crystal surface. Since almost all the excitons incident on the surface result in luminescence of the molecules of the primary (host) material, then a decrease in the film thickness should lead to an increase in B_a/B_n. The increase in B_a/B_n in thick anthracene crystals as the film thickness diminishes is related to the decrease in reabsorption of fluorescence radiation by anthracene. The magnitude of the impurity concentration influences this effect substantially. For very low impurity concentrations (about 10^{-6} mole/mole), the excitons practically completely produce luminescence of the molecules of the primary material (the probability of their capture by an impurity is small). Consequently, under these conditions the reabsorption, which leads to the transformation of shortwave photons of anthracene luminescence into excitons, will affect the quantum efficiency of anthracene luminescence only slightly. But in the presence of high anthracene emission, reabsorption leads to a significant increase in the number of excitons and, therefore, to the growth of the quantum efficiency of the naphthacene luminescence, which is proportional to the total quantity of excitons.

Hence, it would be expected that a diminution in the film thickness and, therefore, a diminution in the reabsorption will influence the quantum efficiency of anthracene slightly and the quantum efficiency of naphthacene luminescence strongly for very low impurity concentrations.

The main amount of the excitons is trapped by the impurity for high impurity concentrations. Since only a small part of the excitons being formed because of the reabsorption is emitted by the molecules of the primary material in this case, then the quantum efficiency of the anthracene should diminish as the crystal thickness increases, i.e., as reabsorption increases. Conversely, the quantum efficiency of naphthacene* should depend slightly on the crystal thickness. Actually, the emission of the primary material is small for high impurity concentrations and, consequently reabsorption of part of the photons of this emission influences the total number of excitons and, therefore, the quantum efficiency of naphthacene, very slightly.

Hence, in contrast to crystals with a low impurity concentration, the quantum efficiency of naphthacene for crystals with high impurity concentration should change slightly as the crystal thickness changes, but the change in the quantum efficiency of anthracene is significant.

A quantitative computation can be made on the basis, proposed by one of the authors [3], of the theory of the diffusion motion of excitons. Such a computation is presented in [1] for thin films. A comparison of the theoretical values of B_a/B_n with experimental results, presented in the cited work, shows that the theory yields the correct dependence of the change in the quantum efficiencies on the impurity concentration for a decrease in crystal thickness. Theoretical values of B_a/B_n for the impurity concentrations investigated agree with experimental values within 20%.

In the case of thick crystals, it is necessary to take into account reabsorption by anthracene of fluorescence luminescence. Appropriate computations are given in [4]. In this case, also, the theoretical formulas describe well enough the experimentally established concentration dependence of the influence of reabsorption on the quantum efficiency of luminescence of the primary material and the impurity.

May 29, 1958

References

1. A. N. Faidysh: Opt. i Spekt. 4, No. 5, 1958
2. A. N. Faidysh (In press)
3. I. IA. Kucherov, O. M. Faidysh: Dop. AN Ukr. SSR, 1, 61, 1956
4. O. M. Faidysh, L. IU. Chechik: Ukr. Phys. Journ., 3, 27, 1958

*Editor's Note: for high impurity concentration.

TOM VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar' , 1959
VOL. VI, No. 1 OPTICS AND SPECTROSCOPY January , 1959

Influence Of The Internal Field on Raman Spectrum Intensity

V. M. PIVOVAROV

A phenomenological explanation of the anomalous concentration behavior of the combination scattering line intensity of the components of a number of binary mixtures has been proposed by Pivovarov and Kislovskii in [1]. This explanation is based on definite assumptions on the relation between the position and intensity of the absorption bands, which are essential for combination scattering, with the value of refractive index in the region of the absorption band.

Another viewpoint in the consideration of the problem is also possible. As is known, a change in the refractive index of the medium causes a change in the field intensity of the light wave affecting the molecule situated in this medium. It is essential to note that this change is determined, in the combination scattering case, by the refractive index in the wavelength band of the scattered radiation. Consequently, it would be meaningful to consider the question of how the influence of the internal field on the relative combination scattering line intensity can be taken into account. One of the possibilities reduces to the introduction of a system of oscillators with frequencies ν_{0e}, which is equivalent to a set of electronic transitions in the molecule, and to the consideration of the influence of the internal field thereon according to Onsager [2]. In this case, as Bayliss [3] showed, a change in the vibration frequency of the electronic oscillator is related to the refractive index thus

$$\Delta\nu_{0e} \sim -\frac{P_{0e}}{r^3}\cdot\frac{n^2-1}{2n^2+1}, \tag{1}$$

where P_{0e} is a matrix element of the electronic transition, n the refractive index, r the radius of the molecular sphere. According to semi-classical theory [4], the combination scattering intensity can be defined as follows:

$$J \sim E^2(n)_{eff}\,(5b'^2 + 13g'^2), \tag{2}$$

where b', the trace of the tensor of the derivative of the polarization with respect to the normal vibration coordinate q , is written as

$$b' = \sum_{i=\xi,\eta,\zeta}\sum_{e}\frac{2\left[(\nu_{0e}+\Delta\nu_{0e})^2+\nu^2\right]}{\left[(\nu_{0e}+\Delta\nu_{0e})^2-\nu^2\right]^2}\left|(P_i)_{0e}\right|^2_{q_0}\left(\frac{\partial\nu_{0e}}{\partial q}\right)_{q_0}, \tag{3}$$

and g' , the anisotropy of this same tensor, is

$$g' = \left|\frac{1}{2}\left[\sum_{i,j=\xi,\eta,\zeta}\sum_{e}\frac{2\left[(\nu_{0e}+\Delta\nu_{0e})^2+\nu^2\right]}{\left[(\nu_{0e}+\Delta\nu_{0e})^2-\nu^2\right]^2}\left(\left|(P_i)_{0e}\right|^2_{q_0}-\left|(P_j)_{0e}\right|^2_{q_0}\right)\left(\frac{\partial\nu_{0e}}{\partial q}\right)_{q_0}\right]^2\right|^{\frac{1}{2}} \tag{4}$$

Here, ξ , η , ζ are the principal axes of the tensor of the derivative of the polarization, ν is the frequency of the exciting light.

It is seen from the expressions presented that the combination scattering line intensity will increase as the refractive index of the medium increases since the frequency factor and $E(n)_{eff}$ will both increase. The intensity of the depolarized lines, dependent on the anisotropy g', must here vary greater, as a rule, than does the polarized line intensity, dependent on the trace b' .

Another possibility in the consideration of the phenomenon is the following. Let the molecule have three main polarizations $a_\xi(q)$, $a_\eta(q)$ and $a_\zeta(q)$, where q is the set of normal vibrational coordinates. If such an anisotropic, vibrating molecule is placed in a medium with the refractive index n , then the electric field with the intensity $E(q)_{eff}$ induces the following moment therein:

$$p_\xi(q) = a_\xi(q)\,E(q)_{eff}, \tag{5}$$

where, according to Onsager,

$$E(q)_{eff} = \frac{3n^2}{2n^2+1}E + \frac{2(n^2-1)}{2n^2+1}\cdot\frac{p_\xi(q)}{r^3}. \tag{6}$$

Substituting the value of $E(q)_{eff}$ in (5) , we obtain the following expression for the induced moment

$$p_\xi(q) = \frac{3n^2 a_\xi(q)\,r^3}{(2n^2+1)\,r^3 - 2(n^2-1)\,a_\xi(q)}E. \tag{7}$$

Hence, a value for the "effective" polarization $a_\xi(q)_{eff}$ can be obtained /5/:

$$a_\xi(q)_{eff} = \frac{3n^2 a_\xi(q)\,r^3}{(2n^2+1)\,r^3 - 2(n^2-1)\,a_\xi(q)}. \tag{8}$$

According to semi-classical theory [4], the combination scattering line intensity is proportional to the square of the matrix element of the derivative of the polarizability with respect to the normal coordinate. In our case the derivative of the "effective" polarization equals

$$\left(\frac{\partial a_\xi(q)_{eff}}{\partial q}\right)_{q_0} = \frac{3n^2(2n^2+1)\,r^6}{\left[(2n^2+1)\,r^3 - 2(n^2-1)\,a_\xi(q_0)\right]^2}\left(\frac{\partial a_\xi(q)}{\partial q}\right)_{q_0}, \tag{9}$$

where $\left(\frac{\partial a_\xi(q)}{\partial q}\right)_{q_0}$ is the derivative of the polarization without taking the influence of the medium into account. A valence-optical scheme can be used to compute the $\left(\frac{\partial a_\xi(q)_{eff}}{\partial q}\right)_{q_0}$ of complex molecules.

Hence, it is not difficult to be convinced that the trace b'_{eff} and the anisotropy g'_{eff} increase as n increases, where the relative change in g'_{eff} is usually greater than in b'_{eff}.

Both the models proposed describe known experimental facts qualitatively correctly, in particular, that the depolarized lines are subjected to anomalies in the intensity to a larger degree than are the polarized lines [6,7]. Hence, the concentration dependence, studied in [6,7], of the intensity in the spectra of binary mixtures whose components have substantially different refractive indices (acetone, carbon tetrachloride, chloroform, benzene, etc.) can be described within the framework of the notion of the reactive internal field of the medium.

In order to eliminate the influence of the medium, which is transmitted by the refractive index, we measured the coefficient of the intensity of the 1707 cm^{-1} line of pure acetone and of 50% mixtures (by volume) with carbon tetrachloride and with n-hexane. The refractive indices of acetone and the latter substance are approximately equal. It appear that although deviations from the proportionality of the dependence of the investigated line intensity on the concentration are observed in the mixture of ace tone with n - hexane, these deviations are nevertheless 5- 10 times smaller than in the mixture with carbon tetrachloride and they are still within the

mits of accuracy of the measurements. The re-
lts of these experiments verify the conceptions
developed. Moreover, that the Onsager model is
adequate to describe all the details of the phe-
menon has not been excluded. As is known, this
del is not applicable to cases of intense intra-
lecular interaction which accompanies the asso-
ation of molecules, for example, the formation of
mplex compounds by means of a hydrogen bond,
ce. As yet it is impossible to explain the ano-
lies in the combination scattering intensity,
served in these cases, by the influence of the
nternal field of the medium. They can be ex-
ained on the basis of an analysis of the para-
eters which actually exist for the absorption
and of combination scattering.

In conclusion, I am grateful to IA.S. Bobo-
ich and to B.S. Neporent for interest and atten-
ion to the research.

June 2, 1958

References

1. V. M. PIVOVAROV, L. D. KISLOVSKII: Opt. i Spektr. 5, 251 (1958)
2. L. ONSAGER: J. Am. Chem. Soc. 58, 1986 (1936)
3. N.S. BAYLISS: J. Chem. Phys. 18, 292 (1950)
4. M. V. VOL'KENSHTEIN, M. A. EL'IASHEVICH, B. I. STEPANOV: Vibration of Molecules, vol. 2, GITTL, Moscow,(1949)
5. A. I. FRENKEL': Kinetic Theory of Fluids, moscow-Leningrad, (1945)
6. IA. S. BOBOVICH, T. P. TULUB: ZETF 30, 189 (1955)(See translation in Sov. Phys. JETP)
7. V.M. PIVOVAROV, IA. S. BOBOVICH: Opti i Spektr. 3, 134 (1957)

TOM VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar', 1959
VOL. VI, No. 1 OPTICS AND SPECTROSCOPY January, 1959

On the Question of the "Ballistic" Method to Investigate the Decay of Phosphorescence

M. G. KAMINSKII

Among the work devoted to an investigation of the decay of phosphorescence by photoelectric methods, the so-called "ballistic" method developed by B. A. Piatnitskii has been somewhat widely received.

As in the usual ballistic method, the observation of the decay is made after a single excitation of given duration. The diminishing brightness of the luminescence is measured by using a photocell with a mirror galvanometer in the aperiodic region close to critical.

The phosphorescent light is directed at the photocell for a definite time interval t_1 after the excitation has ceased (after 1 sec, for example) and the maximum deflection $\varphi_m(t_1)$ is measured. After the luminescence of the phosphor has ceased, there is a second excitation and the maximum deflection $\varphi_m(t_2)$ is measured through a second time interval t_2 after the cessation of the excitation (after 2 sec, say), etc. It has here been assumed that the galvanometer yields ballistic deflections proportional to the luminous sum at the end of each second of decay.

As follows from the theory of the ballistic galvanometer, the deflection is proportional, to 1% accuracy, to the quantity of electricity only if the effective time on the galvanometer* does not exceed $0.07T_0$, where T_0 is the period of free vibration of the galvanometer [1]. In the case of a simple exponential decay such as $i(t) = i_0 e^{-\alpha t}$, it can be considered in practice that the effective time does not exceed the time $t' = \frac{7}{\alpha}$ during which the luminescence will decay approximately 1000 times. Hence, in the case of an exponential decay, the galvanometer yields a ballistic deflection only for compliance with the condition $\alpha \geq \frac{100}{T_0}$.

Piatnitskii, Vishnevskii, Tepliakov [2-4] use the method of measurement usual for the ballistic method at $\alpha \ll \frac{100}{T_0}$, assuming erroneously that the galvanometer in this case also yields "ballistic deflections proportional to the intensity and the luminous sum at the end of each second of decay" [5]. The statement of the proportionality of the intensity to the luminous sum (valid just for exponential decay) has been extended by a number of authors [3-6], completely without foundation, to the case for example of damping according to a more complex law determined by the sum of two exponentials.

Let us show that the maximum deflection $\varphi_m(tk)$ under the long effect of photocurrent on the galvanometer does not compare with any of the parameters of the damping function, with the exception perhaps of the simple exponential damping case, even then with well-known limitations.

1. For simple exponential damping $i(t) = i_0 e^{-\alpha t}$, the value of the maximum deflection of the galvanometer in the critically damped case is defined by the expression (see Appendix):

$$\varphi_m(t_k) = \gamma_i \frac{\omega_0^2}{(\omega_0 - \alpha)^2} \left\{ e^{-\alpha \tau_m} - [(\omega_0 - \alpha)\tau_m + 1] e^{-\omega_0 \tau_m} \right\} i_0 e^{-\alpha t_k}, \quad (1)$$

where ω_0 is the angular frequency of the galvanometer free oscillations; γ_i is the galvanometer response to direct current, t_k is the instant at which the photocell starts to be exposed, τ_m is the instant the galvanometer coil achieves its maximum deviation as measured from the start of the photocell exposure t_k.

As follows from (1), the maximum deflection $\varphi_m(t_k)$ is actually proportional to the intensity of luminescence $i(t_k) = i_0 e^{-\alpha t_k}$. However, the proportionality coefficient $\gamma = \frac{\varphi_m(t_k)}{i(t_k)}$, which is the galvanometer sensitivity for the given method of measurement, depends substantially on the decay exponent α.

The result of computing the ratio γ/γ_i for various α and ω_0 is shown in Table 1. Analysis of the data presented in Table 1 shows that a comparison of the initial intensities of phosphors with different α, existing in a number of works [3,5,6,9-11], is inadmissible without additional conversion since it can lead to erroneous conclusions. It is also hardly possible to establish a dependence of the initial intensities on some one of the factors (temperature, say), as certain authors do [7,8,12,13], if α also varies here.

2. For damping by a more complex law, the quantity γ becomes dependent on the time t_k, which violates the proportionality between the photocurrent $i(t_k)$ and the functions $\varphi_m(t_k)$ obtained as a result of measurements.

Let us consider the case when $i(t) = i_{01} e^{-\alpha_1 t} + i_{02} e^{-\alpha_2 t}$. The response will be determined by the expression

$$\gamma = \gamma_i \omega_0^2 \frac{\frac{i_{01} e^{-\alpha_1 t_k}}{(\alpha_1 - \omega_0)^2} \left\{ e^{-\alpha_1 \tau_m} - [(\omega_0 - \alpha_1)\tau_m + 1] e^{-\omega_0 \tau_m} \right\}}{i_{10} e^{-\alpha_1 t_k} + i_{02} e^{-\alpha_2 t_k}} + \quad (2)$$

$$+ \gamma_i \omega_0^2 \frac{\frac{i_{02} e^{-\alpha_2 t_k}}{(\alpha_2 - \omega_0)^2} \left\{ e^{-\alpha_2 \tau_m} - [(\omega_0 - \alpha_2)\tau_m + 1] e^{-\omega_0 \tau_m} \right\}}{i_{01} e^{-\alpha_1 t_k} + i_{02} e^{-\alpha_2 t_k}}$$

As follows from (2), the sensitivity γ depends not only on α_1 and α_2 but also on the time which the photocell starts to be exposed t_k. Values of the ratio γ/γ_i are shown in Table 2 for prescribed α_1, α_2 and ω_0 ($\alpha_1 = 3.5$, $\alpha_2 = 0.5$, $\omega_0 = 4$, $i_{01} = i_{02}$). An analysis of the results presented in Table 2 indicates that the function $\varphi_m(t_k$ obtained as a result of measurement differs substantially from the actual decay law $i(t)$.* Consequently, use of the "ballistic" method, such as

*Editor's Note: i.e., the time which the current is applied. AWW.

*In light of the above, the fact of the agreement of the decay law of a number of substances, as found experimentally by certain authors (say [14]), with the decay law obtained theoretically by S. I. VAVILOV which has the form

$$J(t) = \frac{N^2 e^{-\alpha N t} \left(1 + \frac{N}{n_0}\right)}{\left(1 + \frac{N}{n_0} - e^{-\alpha N t}\right)^2} \quad (3)$$

is rather unexpected. This agreement seems to be all the more unexpected, since (3), in the terminology of S. I. Vavilov, is an elementary decay law and has been obtained under the assumption that the duration of the excitation is small [15,16]. The duration of the excitation in the measurements made by the authors mentioned was large.

rtain authors use [3,6,12,14], to investigate the ay of luminescence, which occurs not according to e simple exponential law, is not admissible.

Table 1

riod of ee Osc. the lvano- ter (Sec.)	Angular Freq. of the Galvanometer $\omega_0 = \frac{2\pi}{T_0}(\frac{1}{\text{Sec.}})$	Size of the Decay Exponent under Investigation $\alpha(\frac{1}{\text{sec.}})$	Time of Reaching Max. Deflection τ_m(Sec.)	Ratio of "Ballistic" Sensitivity to Direct Current Sensitivity γ/γ_i
6.28	1	0.19	3.39	0.61
		0.30	2.95	0.50
		0.50	2.54	0.41
		0.70	2.33	0.34
		1.10	1.94	0.23
12	0.52	0.35[7]	4.40	0.34
		0.47[8]	4.10	0.29
		0.62[7]	3.70	0.24
		0.93[8]	3.18	0.18

Table 2

	t_k					
	0	0,5	1	2	6	10
γ/γ_i . .	0.45	0.58	0.67	0.70	0.70	0.70
m . . .	0.74	0.90	0.93	0.94	0.94	0.94

3. When the decay process is defined by the um of two exponentials, then the build-up of both uminescence components is possible by means of the otal curve. However, the difficulty in this operation increases significantly if α_1 and α_2 differ nly slightly. Particularly large errors occur in hose cases when the nearness in the decay exponents ($\alpha_1 = 1.5\alpha_2$, for example) is combined with the eakness of the longer luminescence ($i_{01} = 10i_{02}$, ay). Under these conditions, it is easy to arrive at the erroneous conclusion that the decay occurs according to a simple exponential law even when the method of measurement guarantees proportionality between the galvanometer and photocurrent readings [17].

The nature of the dependence of γ on t_k shows that the probability of committing this error under the conditions of the "ballistic" method increases to a significant degree. This last fact depreciates the results to a known degree even in those cases when the decay law has been obtained as a simple exponential.

APPENDIX

The relation between the angle of rotation of the galvanometer and the current is found by solving the equation of motion of the movable system of the galvanometer. This equation is

$$\frac{d^2\varphi}{d\tau^2} + \frac{b}{I}\cdot\frac{d\varphi}{d\tau} + \frac{D}{I}\varphi = \frac{q}{I}\,i(\tau); \quad \varphi(0)=0; \quad \varphi'(0)=0; \tag{4}$$

where φ is the angle of rotation of the galvanometer, I the moment of inertia of the galvanometer coil, D the suspension torsion constant, b the damping coefficient, q the galvanometer dynamic constant, τ the time measured from the instant the photocell begins to be exposed $\tau = t - t_k$, where t is the time measured from the instant excitation ceases, t_k is the moment the photocell starts to be exposed, $i(\tau)$ is the photocurrent under investigation.

1. If the decay occurs according to a simple exponential $i(\tau) = i_{ok}e^{-\alpha\tau}$ where $i_{ok} = i_o e^{-\alpha t_k}$, then the solution of (4) will be

$$\varphi(\tau) = \gamma_i \frac{\omega_0^2}{(\alpha-\omega_0)^2}\left\{e^{-\alpha\tau} - [(\omega_0-\alpha)\tau+1]\,e^{-\omega_0\tau}\right\} i_0 e^{-\alpha t_k}; \quad \frac{q}{D} = \gamma_i. \tag{5}$$

Finding τ_m from the condition of a maximum for (5), we obtain the value of the maximum deflection (1).

2. When the decay law is defined by the sum of two exponentials, the solution of (4) is:

$$\varphi(\tau) = \gamma_i\,\omega_0^2\left\{\frac{i_{01}e^{-\alpha_1 t_k}}{(\alpha_1-\omega_0)^2}\left[e^{-\alpha_1\tau_m} + (\alpha_i\omega_0)\,\tau_m e^{-\omega_0\tau_m} - e^{-\omega_0\tau_m}\right] + \right.$$
$$\left. + \frac{i_{02}e^{-\alpha_2 t_k}}{(\alpha_2-\omega_0)^2}\left[e^{-\alpha_2\tau_m} - (\alpha_2-\omega_0)\,\tau_m e^{-\omega_0\tau_m} - e^{-\omega_0\tau_m}\right]\right\}. \tag{6}$$

Finding τ_m from the condition of a maximum for (6), and dividing the value of the maximum deflection obtained at the instant t_k by the value of the photocurrent at this instant, we obtain (2).

June 16, 1958

References

1. O. Verner: Chuvstvitel'nye gal'vanometry postoiannogo i peremennogo toka (Sensitive dc and ac galvanometers) Leningrad, 1933
2. B. A. Piatnitskii: ZETF, 9, 310, (1939)
3. P. A. Tepliakov: Opt. i Spektr., 1, 896, (1956)
4. A. P. Vishnevskii: DAN USSR, 63, 503, (1948)
5. B. A. Piatnitskii: DAN USSR, 57, 711, (1947)
6. P. A. Tepliakov, B. A. Piatnitskii: Izv., AN USSR, Phys. ser., 20, 524, (1956) (See Bulletin, Physics series of Columbia Technical Translations)
7. B. A. Piatnitskii, T. P. Vinokurova: DAN USSR, 68, 483, (1949)
8. B. A. Piatnitskii: DAN USSR, 62, 59, (1948)
9. B. A. Piatnitskii: DAN USSR, 64, 813, (1948)
10. B. A. Piatnitskii: DAN USSR, 71, 457, (1950)
11. O. G. Zinov'eva: DAN USSR, 68, 265, (1949)
12. B. A. Piatnitskii, M. S. Fadeeva: Izv., AN USSR, Phys. ser., 20, 520, (1956) (See Bulletin, Phys. ser., of Columbia Technical Translations)
13. B. A. Piatnitskii: Izv., AN USSR, Phys. ser., 15, (1951)
14. B. A. Piatnitskii: ZETF, 9, 1351, (1939)
15. S. I. Vavilov: Phys. Z. Sowjetunion, 5, 369, (1934)
16. S. I. Vavilov: DAN USSR, 27, 112, (1940)
17. V. I. Levshin: Fotoliuminestsentsiia Zhidkikh i Tverdykh Veshchestv (Photoluminescence of Liquid and Solid Substances), Moscow, GITTL, 1951

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

Infrared Absorption Spectrum of Cuprous Oxide

I. PASTRNIAK

The absorption spectrum of cuprous oxide in the infrared region to 15μ was first studied by Gross and Karryev [1]. Two absorption maxima were found at wavelengths of 8.9μ (1124 cm^{-1}) and 12.6μ (794 cm^{-1}). In subsequent investigations, Gross and Zakharchenia turned attention to the fact that the frequency of the first of these macima (1124 cm^{-1}) agrees with the difference in the frequencies of the boundaries of the two hydrogen-like series of absorption lines of an exciton in cuprous oxide [2]. It is possible that this and other peculiarities of the structure of the intrinsic absorption edge of this semiconductor are specified by the interaction of electronic transitions with lattice vibrations. In this connection, the problem arises of a more detailed study of the vibrational spectrum of the cuprous oxide lattice. The present research is intended to continue the investigation of the absorption spectrum in the range to 25μ.

Absorption curves were recorded on cuprous oxide samples prepared by the usual method, the oxidation of a copper plate and its subsequent annealing under a definite oxygen pressure whereby the desired content of super-stoichiometric oxygen is acheived. Plates of 30 - 1500μ thickness are prepared from the samples obtained by sectioning. The investigations in the region of intense absorption were conducted on cuprous oxide films fractions of a micron thick. It should be noted that fine cuprous oxide films, obtained by the oxidation of copper deposited on a substrate, have a more imperfect lattice, moreover, their stoichiometry in not determined exactly. Consequently, the investigations in the intense absorption band were conducted in in parallel, also on samples prepared from powdered Cu_2O pressed into KBr. The majority of curves was recorded on samples obtained by sectioning of cuprous oxide plates.

The IKS-11 spectrograph with NaCl, KCl and KBr prisms was used as the spectrum analyzer. Certain curves were recorded on the double IKS-14 spectrograph.

The crystal lattice of cuprous oxide, belonging to the space group O_h^4, contains two oxygen ions in the elementary cell at sites having the symmetry T_d and four copper ions at sites with symmetry D_{3d}. Using group theory, it can be shown that the vibrational spectrum of cuprous oxide must contain two triply degenerate optical branches of the vibrations active in infrared absorption, 1 triple degenerate optical branch of the vibrations active in the Raman spectrum as well as 1 triple, 1 double degenerate and 1 nondegenerate optical branch of the vibrations active in neither infrared absorption nor in the Raman effect. If the deviations from harmonic vibrations are taken into account, the presence of combination frequencies, whose absorption coefficient is considerably less than for the optically active frequencies can also be expected in the absorption spectrum.

The absorption curve of cuprous oxide is shown in figure 1, where the values of the transmission are plotted along the vertical axis. The frequencies corresponding to the absorption maximums are presented in the table along with the designations. The position of the maxima No. 3,5,8,9,10, has been determined to 5 cm^{-1} accuracy because of their relative width or because they overlap with other maxima.

No.	λ (in μ)	ν (in cm^{-1})	E(eV)	Intensity	Designation
1	7.65	1307	0.162	V.W.	$\nu_1+\nu_6$
2	8.90	1124	0.139	W.	ν_1
3	11.8	848	0.105	W.	$\nu_3+\nu_6$
4	12.6	794	0.0985	W.	$\nu_4+\nu_6$
5	14.3	699	0.087	W.	ν_2
6	15.1	662	0.082	S.	ν_3
7	16.4	610	0.076	S.	ν_4
8	19.3	518	0.064	W.	ν_5
9	20.6	485	0.060	W.	$\nu_3-\nu_5$
10	23.3	429	0.053	W.	$\nu_4-\nu_5$
11	—	182	0.023	-	ν_6

Remark: v.w.- very weak, w.- weak, s.- strong.

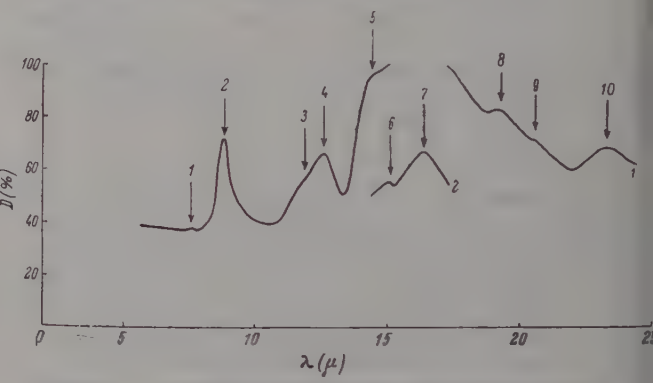


Figure 1. Cuprous oxide absorption curve in the range to 25 μ.

1 - Sample 30μ thick; 2 - sample of powdered Cu_2O pressed into KBr, thickness of Cu_2O film, 1μ.

The presence of two absorption maxima is seen on curve 2 (fig. 1) at 15.1 and 16.4 μ (No. 6, 7), where the absorption coefficient has the order of magnitude 10^3 - 10^4 cm^{-1} and is comparable to the absorption coefficient in the vibrational spectra of alkali-halide crystals. Apparently these maxima correspond to two optical branches of the vibrational spectrum active in infrared absorption. The absorption coefficients at the remaining maxima have the order of magnitude 100 cm^{-1}, in fact 10 cm^{-1} at the maxim um at 7.6 μ.

Of particular interest is the absorption maximum at 8.9 μ (ν = 1124 cm^{-1}), whose frequency is in agreement with the difference in the frequencies between the boundaries of the series of absorption lines of the exciton in cuprous oxide [2].

Three viewpoints, which can relate to infrared absorption, have been expressed to explain the presence of these two series up to now. The

pinion is expressed by Elliott in [3] that their resence is related to the structure of the valnce band, which occurs because of the reduction f the triple degeneracy of this band due to spinrbital interaction. Pavinskii [4] assumes that he presence of the two series is specified by he possibility of two states of holes in the uprous oxide crystal with differing energies odd and even) relative to the center of inverion, the copper ion. This would also lead to the ppearance of the structure of the valence band. ikitine et al. consider that one of the exciton eries is a vibrational satellite of the other, hat simultaneous absorption of a photon [5] occurs during the absorption in the "yellow" series.

If the agreement of the frequency of the absorption maximum with the 8.9 μ wavelengths and he difference of the frequencies of the boundaries f the exciton series is not considered random and f the first two viewpoints are valid then we should bserve a dependence of the absorption intensity t this maximum on the concentration of the free oles. It has been established, by measurement in amples with different excess oxygen content and herefore, with different conductivity, that the agnitude of the absorption coefficient at this aximum is independent of the free hole concentraion, which is confirmed also by the temperature dependence of the absorption at this maximum (fig.). As the temperature is reduced to - 110° C , he maximum shifts toward the shortwave length by .11 μ and its half-width diminishes but the toal absorption intensity, which is expressed by he area bounded by the absorption curve, does not hange. At the same time, the free hole concentraion, as is known from measurements of the electrial conduction and the Hall effect, drops by sevral orders.

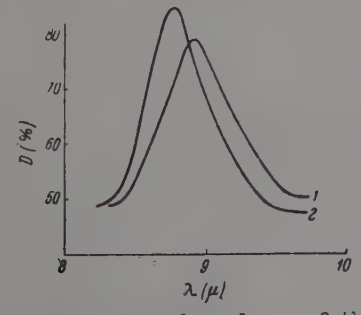


Figure 2. Temperature dependence of the absorption at the 8.9 μ maximum.
1 - T = 20° C ; 2 - T = - 110° C

Absorption curves were also recorded on n-type cuprous oxide samples, which were obtained by introducing Zn or Cd impurities. No change in the absorption intensity was observed in this case either.

The independence of the maximum $\lambda = 8.9$ μ from the impurities and the concentration of free holes and its stability in all the samples investigated permits the statement to be made that this maximum belongs to one of the frequencies of the vibrational spectrum of the crystal. The fact that there is a low intensity absorption maximum at the wavelength 7.6 μ along with the 8.9 μ maximum and which can be designated as a total intensity with the frequency $\nu = 1184 - 182$ cm^{-1} is also indicative. The appearance of combination frequencies in absorption is not observed for impurity maximums.

The maximums at the wavelengths 11.8, 12.6, 20.6 and 23.3 μ can also be designated as combinations. The magnitude of the absorption coefficients at these maxima is several tenths of a cm^{-1} . The absorption corresponding to the frequency $\nu = 182$ cm^{-1} , which is encountered in the combination frequencies, must lie at 55 μ , i.e., in a range which has not been investigated. Apparently, this frequency corresponds to the vibrational branch which is inactive in the infrared absorption but is active in the Raman spectrum since, according to the rule of selection for combination frequencies, the appearance of an appropriate maximum in absorption is more probable in this case.

The occurrence of maxima at 14.3 and 19.3μ has not been explained. The maximum at 14.3 μ , which is expressed particularly sharply in the atomized samples (it could not be detected successfully on all the samples obtained by sectioning), is related either to lattice defects or, just as is the maximum at 19.3 μ , belongs to the vibrational branch of the crystal which is inactive in absorption. Indicative of this is that the difference in the frequencies between these maxima equals 181 cm^{-1} , just as for other composite frequencies.

How completely the vibrational spectrum of the cuprous oxide crystal has been clarified herein, will be shown by further investigations in the longer wave band of the spectrum. They also permit the frequencies observed to be compared to possible types of lattice vibrations.

In conclusion, I am grateful to E. F. Gross for proposing the topic and for valuable assistance in the research and for discussing the results. I am also grateful to A. I. Stekhanov and P. P. Pavinskii for many valuable comments.

June 18, 1958

References

1. E. F. GROSS, N. A. KARRYEV: DAN USSR, 84, 261, (1952).
2. E. F. GROSS, B. P. ZAKHARCHENIA: DAN USST, 90, 745, (1953).
3. R. J. ELLIOTT: Phys. Rev., 108, 1384, (1958).
4. P. P. PAVINSKII, A. G. ZHILICH: Vestnik, Leningrad Univ., No. 4, Issue 1, 50, (1957).
5. S. NIKITINE, G. PERNY: M. SIESKIND: C. R., 238, 67, (1954).

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

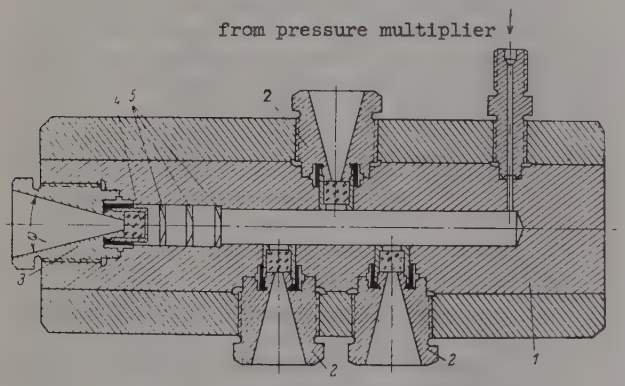
Ianvar' , 1959
January , 1959

Production of Raman Spectra at High Pressures

M. G. GONIKBERG, KH. E. STERIN, S. A. UKHOLIN, A. A. OPEKUNOV, V. T. ALEKSANIAN

The investigation of vibrational spectra at high pressures is of considerable interest as a way of obtaining new information on molecular interactions as well as on possible molecular deformations. In recent years papers [1-4] have been published which are devoted to the study of infrared absorption spectra at high and ultra-high pressure. The lack of investigations on Raman spectra of liquid and gaseous substances at high pressures is apparently explained by technical difficulties, related primarily to the necessity of introducing a considerable luminous flux into the high-pressure chamber.

In order to produce Raman spectra at pressures up to 2500 kg/cm^2 , we used the apparatus described herein. The scattering cell 1 (see sketch) consists of two steel cylinders one fitting within the other; the outer diameter of the external cylinder was 160 mm and the diameter of the inner chamber was 20 mm. The substance enclosed within the cell 1 was illuminated through three windows 2 located perpendicularly to the cell axis; the window 3 was used to observe the scattered light. The window construction is based on the principle of "uncompensated area" [5]. The glass cylinder 4 (d = 15 mm , l = 15 mm) with optically parallel end surfaces is pressed to the ground surface of the window frame screwed into the receiver 1 with an annular packing. The smallest diameter of the conical window opening is 7 mm ; the angle ϕ is 45°.



Scattering cell.

The Raman spectra were excited by the blue line of mercury: λ = 4538Å. The light from the PRK type lamp was concentrated within the cell 1 with the aid of condensing lenses. Whenever required, light filters were placed in the path of the illuminating beams. The diaphragms 5 were mounted in the path of the dispersed beam in order to eliminate light reflected by the inner walls of the cell.

The receiver, placed on a special pedestal, was arranged on the axis of an ISP-51 spectrograph. The pedestal layout was such as to permit the removal and remounting of the cell without disturbing the adjustment. The spectra were photographed using a camera with F = 120 mm.

Using this apparatus, we obtained the spectra of toluene and isopropylbenzene at pressures of 1000 and 2000 kg/cm^2 . The substances mentioned do not become rigid at these pressures and room temperature and have comparatively strong spectra. Compression was accomplished by using a pressure multiplier. In order to avoid contamination of the fluid during compression, the multiplier piston was packed with a gasket of polytetrafluorethylene. The exposure time was 4 - 6 hours using high-sensitivity plates.

No displacement of the toluene and isopropylbenzene frequencies at the pressures mentioned was observed within the limits of measurement accuracy (1 - 2 cm^{-1}).

The installation described can be used to obtain the spectra of compressed gases also.

July 7, 1958

References

1. E. FISHMAN, H. G. DRICKAMER:
2. R. COULON, L. GALATRY,
3. A. M. BENSON, H. G. DRICKAMER
4. R. A. FITCH, T. E. SLYKHOUSE,
5. P. W. BRIDGMAN: Physics of High Pressures. (Russian Translation, ONTI, 1935)

VI, Vyp. 1 OPTIK I SPEKTROSKOPIIA Ianvar , 1959
. VI, No. 1 OPTICS AND SPECTROSCOPY January , 1959

Production of the Absorption Spectrum of AlO by the Method of Electrically Exploding a Wire in Air at Atmospheric Pressure

V. A. LOGINOV

The possibility is indicated herein of using electrical explosion of a wire in air at atpheric pressure to produce the absorption spectm of AlO . The question of producing molecular ectra by using explosion of wires has been stud- only slightly. Up to now, this phenomenon has been used sufficiently in molecular spectroy. The use and development of this method can d to important practical results.

It is known that the absorption spectrum deds strongly on the intensity of the background. sequently, an important problem is the producn of sources emitting a very bright complex ectrum. The use of condenser discharge through ole in a textolite plate seems to be of pracal value for the production of an impulse source a continous spectrum.

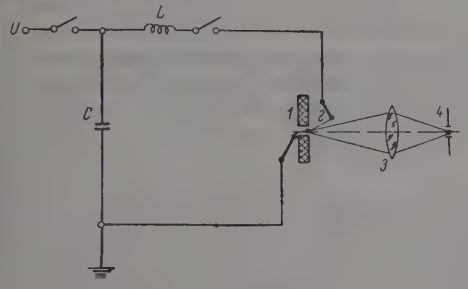


Figure 1. Schematic of the circuit to produce AlO absorption spectra. 1 - Textolite plate with a hole; 2 - wire; 3 - condenser; 4 - slit of the spectrograph; U - high voltage

Anderson [1] discharged a condenser through wire located in the slit of a wooden bar. Hence, n explosion was observed which was accompanied y a bright flash lasting on the order of 10^{-5} ec. Spectroscopic investigations showed that a mplex spectrum had been obtained which included mission and absorption arc lines of the wire matrial. The temperature of the vapors attained 0,000 - 30,000° C as estimated by Anderson from he brightness of the glow.

Ogurtsova and Podmoshenskii [2] established hat if there is a discharge through a hole in a extolite plate, using spectrally pure carbon electrodes, rather than the condenser discharge through wire in a bounded space, then there is produced n impulse source of a complex spectrum which is lmost free of absorption lines in 2500 - 5000 Å ange of the spectrum wavelength.

It has been established experimentally that he discharge radiation can successfully be reduced to the radiation of perfect black body with a rightness temperature on the order of 32,000° K ecause of the significant rise in the pressure in he channel (to 500 atm.), caused by the sudden vaporation of the material of the hole wall, and f the power in comparison with the impulse tubes.

Underlying the method being proposed is the dea of using a condenser discharge through a hole n a textolite plate to generate a source of continous radiation and to use the explosion of a wire in air to produce such a quantity of oxide molecules in a comparatively small volume, as would be adequate to absorb the radiation.

King [3] remarked on the phenomenon of the intense absorption of AlO bands in an electric arc with a current intensity of about 100 amp. in the 4000 - 4900 Å range of the spectrum.

Hori [4], discharging a condenser through aluminum foil in a bounded space and using an asbestos thread saturated with kerosene placed within the region of the foil explosion as the source of a complex spectrum, produced 11 bands of the AlO absorption spectrum which were located in the 4530-5080 Å spectrum range.

Shown in figure 1 is the schematic of the circuit of an apparatus which we have used to produce AlO absorption spectra. One part of the wire is within the hole in the plate (it is necessary to ignite the discharge) and the other is in air (this part of the wire evaporated during the explosion and interacts with the oxygen in the air forming AlO). When a condenser is discharged through a thin wire in the hole of a textolite plate, there occurs an impulse source of continuous radiation with the brightness required to produce AlO absorption spectra.

The thickness of the textolite plate 1 was 12 mm, the hole diameter 3 mm, the diameter of the aluminum wire 2 - 0.15 mm. The axis of the hole coincided with the optical axis of the condenser 3 , consequently, complex radiation along the discharge axis was used. The hole in the textolite plate was reflected by using the condenser 3 near the spectrograph slit 4 . The supply source had the following parameters: C = 36 μF , L = 2 μH . The condenser charging voltage was selected experimentally and could reach values of 7 kV . The spectrograms (fig. 2) were obtained on a two-meter diffraction spectrograph DFS-2 in the first orders of a convex 600 lines/mm grating mounted according to the Pachen-Runge scheme (the reciprocal linear dispersion is of the order of 8.3 Å/mm, the theoretical resolving power in the first orders of the grating is 42,000). Photographic film was used, which is ordinarily used for aerial photographs and has a sensititivity S_d = 0.85 1000 units GOST*

Used as the source of the AlO emission spectrum (fig. 2b) was an aluminum AC ære in air. The AlO emission spectrum was excited by using a DG-1 AC arc generator in the arc region with a 4.5 amp. current. The exposure lasted 10 seconds, the slit width was 0.02 mm.

To produce the AlO absorption spectrum an electrical explosion of an aluminum wire of 0.15 mm diameter in air at atmospheric pressure according to the circuit shown on figure 1 for various charging voltages was used (see the spectrograms c, d and e in fig. 2). The slit width and height were 0.025 and 4 mm , respectively.

The spectrum of an iron arc recorded at a 2 sec exposure in the arc region of the DG-1

* See back cover for list of abbreviations.

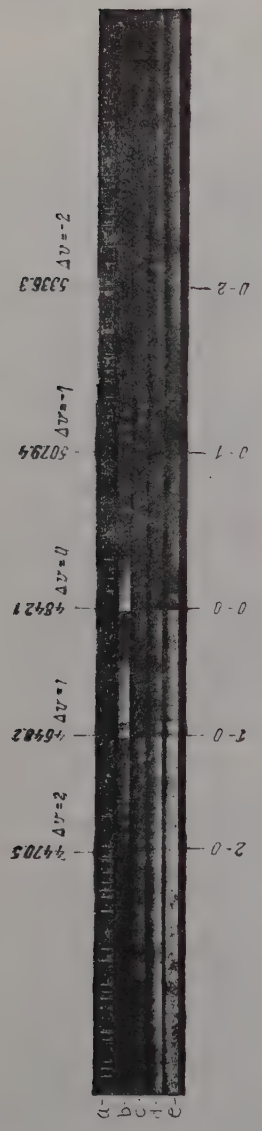


Figure 2. Spectrograms of the system of $2\,X^2$ AlO bands obtained on a DFS-2 spectrograph in the first orders of a 600 lines/mm grating (reciprocal linear dispersion 8.3 /mm).

a - Iron arc comparison spectrum; b - spectrum of an aluminum arc in air; c - AlO absorption spectrum for a U = 2kV charging voltage; d - AlO absorption spectrum for a U = 2,5 kV charging voltage; e - AlO absorption spectrum for a U = 3 kV charging voltage.

with a 4 amp. current (fig. 2a) was used as the comparison spectrum.

The wavelengths of the atomic lines of irom were taken from the table of spectral lines of Zaidel' et al. [5]. The change in the spectrograms was made on an IZA-2 horizontal comparator.

Delander Table of AlO Absorption Band Heads
(values of λ given in)

v'	v''							
	0	1	2	3	4	5	6	7
0	4842.1	5079.4	5336.3	—	—	—	—	—
1	4648.2	4866.4	5102.2	5357.6	—	—	—	—
2	4470.5	4672.0	4889.4	5123.4	5376.6	—	—	—
3	—	4493.9	4694.6	—	5142.4	5394.2	—	—
4	—	4330.5	4516.4	4716.5	—	5161.0	5409.8	—
5	—	—	4352.6	4537.6	4735.5	—	5177.3	5422
6	—	—	—	4373.7	4557.6	—	—	5192
7	—	—	—	—	4393.7	4576.5	—	—
8	—	—	—	—	—	—	—	—
9	—	—	—	—	—	—	4430.3	—
10	—	—	—				—	4446

Presented in the table are numerical values of the wavelengths for 33 AlO absorption band heads located in the visible part of the spectrum (4300 - 5400 Å), which were obtained as a result of using the method cited here.

The numerical values of the band head wavelengths of the table are in good agreement with the values of the emission band head wavelengths in references [6 - 8].

Comparing our results with the results of [8 - 10], we arrive at the obvious conclusion that the system of AlO absorption bands we observed (fig. 2 c, d, e) corresponds to the transition $2\sum^{+} \leftarrow X^2\sum^{+}$, where $X^2\sum^{+}$ is the ground state of AlO.

In conclusion, the author is grateful to V. M. Tatevskii for interest in the research and for useful advice.

July 8, 1958

References

1. J. A. ANDERSON: Astroph. J., 51, 37, (1920).
2. N. N. OGURTSOVA, I. V. PODMOSHENSKII: Opt. i Spektr., 4, 540, (1958).
3. A. S. KING: Astroph., 62, 238, (1925).
4. T. HORI: Sci. Papers Inst. Phys. Chem. Res., Tokyo, 4, 59, (1926).
5. A. N. ZAIDEL', et al.: Tables of Spectral Lines (Tablitsy spektralnykh linii). GITL, Moscow-Leningrad, (1952).
6. G. ERIKSSON, E. HULTHÉN: Z. Phys., 34, 775, (1925).
7. R. MECKE: Phys. Zs., 26, 217, (1925).
8. B. ROSEN: Tables de Constantes et Données Numériques. Paris, 1951.
9. W. C. POMEROY: Phys. Rev., 29, 59, (1927).
10. M. K. SEN: Indian J. Phys., 11, 251, (1937).

DM VI, Vyp. 1
DL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

January , 1959
Ianvar , 1959

On the Infrared Absorption Spectra of Nitrates in Anhydrous Solutions

IA. I. RYSKIN

There is very little information in the literature on the infrared absorption spectra of inorganic salts with complex ions in anhydrous solutions [1]. Moreover, the vibrational spectra can give valuable information on the structure of solutions and on the deformations experienced by ions.

We obtained absorption spectra of a number of nitrate solutions in ketones and ethers. It appears that the influence of the cation on the internal vibrations of the nitrate ion, observed in the crystalline state, is almost completely retained in solutions. In certain cases, when partial dehydration of the salt occurs in an anhydrous medium, the influence mentioned is even amplified.

As an illustration, let us present the vibrational frequency of the NO_3^- anion in fine-crystal cerium nitrate and in ketone solutions of this salt.

Presented in the third line of the table are the vibrational frequencies of the NO_3^- ion, observed in dilute aqueous solutions of nitrates of the alkali metals, in which the influence of the cation is lacking and the anion has D_{3h} symmetry.

The frequency ν_1 of vibrations of the type A_1 in the absorption spectra of nitrates of the alkali (and, mostly, alkali-earth) metals is not active [2]. Its appearance in the spectrum of cerium nitrate can be explained by the influence of the Ce^{3+} cation. This influence is the reason for the splitting of the degenerate (type E) vibration $\nu_{2,4}$. Actually, the perturbations of the vibrations of the NO_3 ion in the cerium nitrate crystal and its solution appear to be very close despite their large value. This indicates the effect of the very same reason for the perturbation in both cases. The fact that the spectrum of this nitrate is almost independent of the type of solvent (ketones, ethers) and nitrates of different metals in the same solvents differ radically in the intensity of the ν_1 vibrations and in the character of the splitting of the $\nu_{2,4}$ vibrations is a further confirmation of the statement on the role of the cation proposed above.

The character of the spectrum of cerium nitrate is that it occupies an intermediate position between nitrates of the alkali metals and anhydrous nitric acid. The latter differs by the covalent character of the bond between the atom of the O' anion and hydrogen [3,4]. Consequently, the multiplicity of the N-O' bond in the $O_2NO'H$ molecule of nitric acid is reduced to 1 and the multiplicity of the two other N-O bonds is raised to 1.5 (in the highly-symmetric nitrate ion, all the N-O bonds have, as is known, the multiplicity $1\frac{1}{3}$). The shell of the $HO'NO_2$ molecule is the point group C_{2v}; its ν_1 vibration is primarily the vibration of the N-O' bond and the $\nu_{2,4}$(E) vibration is split into 2 components which correspond, basically, to the symmetric and anti-symmetric vibrations of the three-point group O-N-O. Here the quantity $\nu_{2,4}$ is larger and the quantity ν_1 is less than the corresponding frequencies of the NO_3 ion.

Using such an analogy, it can be considered that the O'-Me bond (where Me is a metal) is partially covalent for opposite frequency increments $\Delta\bar{\nu}_{2,4}>0$ and $\Delta\nu_1<0$. The frequency ν_1 is 14 cm^{-1} lower than the corresponding frequency of the symmetric ion for cerium nitrate dissolved in methyl ethyl ketone and $\nu_{2,4}$ is 19 cm^{-1} higher than the frequency $\nu_{2,4}$. Therefore the electron cloud of the O' ion is partially displaced toward the cation.

Table

Object	Frequency (cm^{-1})					
	$\nu_{3,5}$	ν_6	ν_1	$\nu_{2,4}$		$\bar{\nu}_{2,4}$
$Ce(NO_3)_3\cdot 6H_2O$ (emulsion in paraffin oil)	735	826	1044	1330	1505	1417
Solution of $Ce(NO_3)_3\cdot 6H_2O$ in methyl ethyl ketone (33%)	736	823	1034	1310	1488	1399
NO_3^- ion (isolated)	720	830	1048 [1]	1380	—	1380

1. The frequency 1048 cm^{-1} for an NO_3^- ion of D_{3H} symmetry is active only in RAman spectra.

The fact is of interest that the $\nu_{2,4}$ and ν_1 bands of cerium nitrate in anhydrous solutions are very narrow. This indicates the absence of significant fluctuation in the mutual locations of the Ce^{3+} and NO_3^- ions. We do not as yet set forth the facts indicating the mutual interaction of anions in solutions. Consequently, it is only possible to speak about the existence of quasimolecular associates of the NO_3^- ions and Ce^{3+}cations in anhydrous solutions at this stage of the investigations. The classification of nitrates according to the character of the influence of the cation on the anion in solutions will be given later in a more complete report.

July 15, 1958

References

1. N. A. Slovokhotova; Zh. Fiz. Khim., 25, 768, (1951).
2. F. A. Miller, C. H. Wilkins: Anal. Chem., 24, 1253, (1952).
3. H. Cohn, C. K. Ingold, H. G. Pool: J. Chem. Soc., 4272, (1952).
4. D. J. Miller, T. R. Morton: Chem. a. Ind., 954, (1956).

TOM VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar', 1959
VOL. VI, No. 1 OPTICS AND SPECTROSCOPY January, 1959

Monocrystals of ZnS and the Spectrum of their Absorption Region at Low Temperatures

E. F. GROSS and L. G. SUSLINA

A study of the optical properties of zinc sulfide crystals is of great interest, since zinc sulfide, activated by various additives (Cu, Ag, Mn, etc.) is a basic material in the preparation of luminofor.

Although there is a vast collection of papers devoted to the zinc sulfide luminofers, comparatively little attention has been paid to the study of pure ZnS, free of intentional additives.

It is known, from studies of the absorption spectrum of ZnS crystals, that the long-wave length region of natural absorption, where the absorption coefficient k increases sharply (from $k \approx 1$ mm^{-1} to $k \approx 10^3$ mm^{-1} in an interval of the order of 70 Å), lies in the neighborhood of 3350 Å, where the maximum photoelectric response occurs [1]. Because of the high value of the absorption coefficient, extremely thin samples are needed for the study of structure of the fundamental absorption.

Brumberg and Pekerman [2], using a specialized method, studied the absorption spectrum of crystals of ZnS at room temperature, and observed two maxima in the natural absorption region, at 3130 and 3340 Å. In addition to these two maxima, Shalimov [3] observed at 77 deg K a third short wave maximum, at 2840 Å, in the spectra of thin films of cubic ZnS prepared by sublimation in a vacuum.

The aim of the present paper is a study of the absorption spectrum of thin single crystals of ZnS, grown by us, at temperatures of 4.2, 77, and 293 deg K.

A number of processes for growing single crystals of ZnS are described in the literature. Among them is the process of sublimating powdered zinc sulfide in a vacuum [4] in the presence of hydrogen [5], and also that of heating ZnS in an atmosphere of hydrogen sulfide [6]. Again, single crystals of ZnS have been prepared by the chemical reaction of zinc with hydrogen sulfide vapor [7,8] and by the same reaction in the presence of hydrogen [9] (Frerichs' method [10]).

In our experimental preparation of single crystals of ZnS the method of heating powdered ZnS in a neutral gas atmosphere was used. This process is analogous to the method used in growing CdS single crystals in the laboratory of S. M. Ryvkin[1]

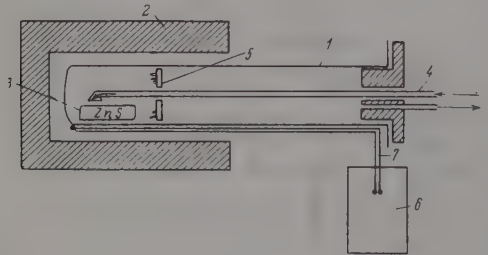


Fig. 1. Apparatus for producing monocrystals of ZnS.

1--reaction tube; 2--electric furnace; 3--boat containing sample; 4--quartz tube for introducing gas; 5--baffles; 6-- thermostat; 7--thermocouple Pt--PtRh.

[1] The authors are deeply indebted to O. A. Matveev and L. V. Maslova for information on this method of growing crystals, and for their advice and assistance.

in the Physico-Technical Institute of the Academy of Sciences of the USSR. In the preparation, a very pure ZnS powder, of the "for luminofor" grade, was used. The heating was carried out in a special apparatus (see Fig. 1), a quartz reaction tube 1 inserted in an electric furnace 2. A quartz boat 3 containing the ZnS was located in the reaction tube at the point of highest temperature, which reached 1270 deg C. Argon, which was used as the neutral atmosphere, was blown over the boat through the quartz tube 4 after having been freed of oxygen (by heating with copper shavings) and after drying over $CaCl_2$ and P_2O_5. Argon was blown into the tube for approximately one hour before the furnace was turned on, in order to expel air from the system. Then the current was switched on, and when the temperature at the boat rose sufficiently the ZnS powder vaporized intensely. The vapors were carried by the stream of argon to the quartz baffles 5. Monocrystals of ZnS were formed on the baffles and on the neighboring walls of the reaction tube.

The crystals were allowed to grow for approximately two hours, after which the furnace was shut off and allowed to cool; the flow of argon was maintained during the entire cooling process.

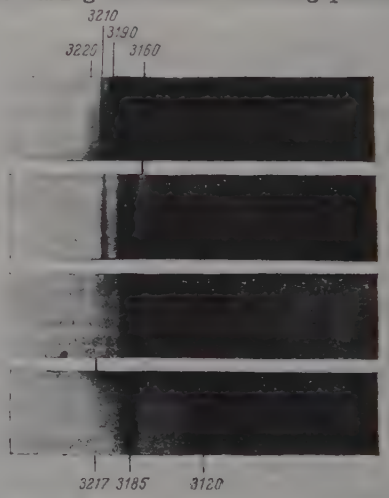


Fig. 2. Spectrograms of the complex structure of the fundamental absorption region of crystals of ZnS.

Thickness of the crystal (approximate) in μ; a -- 10; b -- 1; c -- 1; d -- 0.1. Numbers in the figure denote wave length in Ångstroms.

The form and dimensions of the crystals obtained by this process depend largely on such conditions as the vaporization temperature of the powder, the position of the quartz baffles, the velocity of the gas flow, and the temperature gradient near the baffles. The crystals grown by us were thin colorless plates with maximum dimensions of the order of 25 x 5 mm. The thickness of the plates varied from 0.1 mm to tenths of a micron. Interference colors were very clearly seen in the thinnest microcrystalline plates, having a thickness less than 1 μ.

amination of the plates under a polarization mic-scope showed that they were optically uniaxial l that the optical axis lay in the plane of the ıtelet.

The use of crystals of varying thickness (from veral tens of microns to fractions of a micron) ie possible a thorough study of the long wave nat-al absorption spectrum in the region from 3300 to 00 Å (Fig. 2). Against the background of the con-nuous absorption, rising in the direction of short-wavelengths, we observed a number of narrow ab-rption lines. The clearest definition of the long ve length absorption spectrum was obtained at quid helium temperatures, 4.2 deg K. At this tem-rature, and for plates with a thickness of the der of 10 μ , a narrow absorption band was observ-at about 3190 Å (Fig. 2 a). On the long wave-ngth side of this band there appears a graduated ak continuous absorption, extending to 3220 Å. the graduated region there is a sharp line at 10 Å, and a weaker line at 3217 Å (of half-width Å), which can be observed in Fig. 2 c. The in-nsity of the line at 3210 Å (Fig. 2a) depends on e orientation of the crystal with respect to the cident illuminating ray. This indicates that the ne is polarized. Investigation of even thinner ecimens ($d \approx 1$ μ) allowed us to extend the absorp-on curve further into the short-wave region, where second plateau of continuous absorption was obser-d from 3190 — 3160 Å, and against this background ere was observed a line at 3185 Å with a half-dth approximately 10 Å (Fig. 2 b, 2c). Finally, th the thinnest monocrystals ($d \approx 0.1$ μ), which owed the interference colors, the region of ob-rvation was extended down to $\lambda < 3000$ Å. In is case, it was possible to make a thorough study the short wave line at 3120 Å ($\Delta\lambda \approx 20$ Å) ee Fig. 2 d). In this zone we obseved contin-us absorption, increasing monotonically into the traviolet region.

Heating the crystals from 4.2 to 77 deg K and en to 20 deg C displaces the lines in the direct-on of longer wave lengths and causes them to be-come diffuse. The positions of the absorption lines of ZnS crystals are presented below for various temperatures:

Temperature (°K)	Position of the absorption maximum (Å)		
4.2	3210	3185	3120
77	3220	3190	3130
293	—	3270	3190

Thus, an investigation of the absorption spectrum of ZnS monocrystals has shown that the long wave length decrease in natural absorption of the crystal has a complex structure consisting of a series of lines and also of absorption plateaus.

Added in proof. From a paper by W. W. Piper, P. D. Johnson, and Marple, presented on August 22, 1958, at the conference on semi-conductors held at Rochester, USA, we learned that these authors had independently found a complex structure for the absorption spectrum of ZnS crystals, similar to that observed by us.

July 16, 1958

References

1. W. W. Piper: Phys. Rev., 92, 23 (1953)
2. E. M. Brumberg, F. M. Pekerman: IAN USSR, Phys. ser., 13, 219 (1949).
3. K. Shalimova: Doctoral Dissertation, FIAN USSR, Moscow, 1952.
4. W. W. Piper: J. Chem. Phys., 20, 1343 (1952).
5. W. W. Piper, W. L. Roth: Phys. Rev., 92, 503 (1953).
6. D. C. Reynolds, S. J. Csyzak: Phys. Rev., 79, 543 (1950).
7. E. I. Panasiuk: Report to the VII Conf. on Luminescence. Moscow, 1958.
8. R. Bube: Phys. Rev., 72, 393 (1950).
9. J. Krumbiegel : Naturwiss., 39, 447 (1952).
10. R. Frerichs: Phys. Rev., 72, 594 (1947).

TOM VI, Vyp. 1
VOL. VI, No. 1

O P T I K A I S P E K T R O S K O P I I A
O P T I C S A N D S P E C T R O S C O P Y

Ianvar , 1959
January , 1959

Prolonged Luminescence of Dibenzyl and Diphenylamine Crystals Under Photo- and β - Excitation

T. P. BELIKOVA

Prolonged luminescence of organic substances is connected with the existence of a metastable triplet state. Apparently the same is true of prolonged photoluminescence of organic crystals [1].

The aim of the present investigation was to study the prolonged luminescence of organic crystals under both photo-excitation and excitation by fast electrons.

Electron excitation undoubtedly produces strong ionization, and we may in general expect recombination processes to occur and to influence the decay of the prolonged luminescence [1--3]. Moreover, the conditions of transition to the metastable state may be different under photo- and β-excitation.

As experimental material we chose crystalline substances with strong and sufficiently prolonged post-luminescence at room temperature--namely dibenzyl and diphenylamine. The spectrum of their total luminescence and phosphorescence under photo-excitation was measured with an ISP-51 spectrograph with a central camera.

The spectrum of the phosphorescence of dibenzyl has a strongly marked structure and is displaced toward the longer wavelengths with respect to the spectrum of total luminescence; the phosphorescence spectrum of diphenylamine displayed no structure under the conditions of our experiment, but was also displaced toward the longer wavelengths with respect to the corresponding luminescence spectrum; that is, the so-called β-band of phosphorescence was observed.

For observations of the decay of phosphorescence the specimen was placed in front of the aperture of an FEU-19 photomultiplier; the signal from the photomultiplier was impressed through a cathode follower on the vertical plates of a special oscillograph, with a sweep rate controllable within wide limits. It was thus possible to measure the decay within the region from 0.02 to 50 sec. The input signal was controlled with the aid of a microammeter in series with the oscillograph.

The photo-excitation source was an SVDSh-250 mercury lamp with a UFS-1 filter; the β-particle source was Tl^{204} (strength of the order of 10 mC). A light-shutter was placed between the lamp and the specimen; the shutter for the β-particles was composed of iron plates, which completely absorbed them. An OS-11 filter, with a passband in the yellow-green region, was placed between the specimen and the photomultiplier for better separation of the prolonged luminescence. The decay curves displayed on the oscillograph were photographed. The stationary brightness of the total luminescence was the same for both types of excitation.

Figure 1 represents the oscillogram for dibenzyl. It is evident that the decay curves for phosphorescence are altogether identical. The same result is observed for diphenylamine, in Figure 2.

Fig. 1. Oscillograms of the decay curves for phosphorescence of dibenzyl.
a--photo-excitation, b--β-excitation

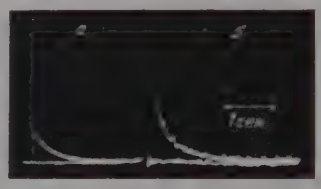


Fig. 2. Oscillograms of the decay curves for phosphorescence of diphenylamine.
a--photo-excitation, b--β-excitation

In both substances the decay curve is exponential, at least in the range of illumination intensities investigated (the intensity was varied by a factor of 50).

The half-life τ was computed from the oscillograms.

For dibenzyl, $\tau = 0.85 \pm 0.02$ sec, and for diphenylamine $\tau = 0.35 \pm 0.02$ sec.

It follows that the recombination processes initiated by β-radiation have no influence on the phosphorescence in the time intervals we observed. Of course, the possibility is not excluded that there are processes specific to hard radiation, with different durations (for example in the microsecond or millisecond range [4,5]).

It follows further from these experiments that for both β-excitation and photo-excitation the transition to the metastable state takes place by the excitation of a singlet state, and that no significant direct excitation of the metastable state was observed.

This work was carried out under the direction of M. D. Galanin, to whom the author expresses his deepest thanks.

June 18, 1958

References

1. H. Kallmann, B. Kramer, E. Sucov. J. Chem. Phys., 23, 1043, (1955).
2. V. A. Iastrebov: ZETF, 21, 164, (1951).
3. V. A. Iastrebov: DAN USSR, 90, 1015, (1953).
4. J. A. Jackson a. F. B. Harrison: Phys. Rev., 89, 322, (1953).
5. K. P. Meyer, A. Maier: Helv. Phys. Acta, 28, 411, (1953).

VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar' , 1959
. VI, No. 1 OPTICS AND SPECTROSCOPY January , 1959

On the Origin of Certain Electronic Transitions in Naphthalene Crystals

A. F. PRIKHOT'KO, M. T. SHPAK

The origin of electronic transitions in naphtha-e has become the subject of many investigations discussions [1]. The origin of an electronic ctrum for crystalline naphthalene is of particu- interest. The contrast of crystal luminescence and absorption at low temperatures and the com- ison of the absorption spectra of vapors and stals permitted us to trace a number of transi- ns to the "purely-crystalline" state. Among se, in particular, were transitions with the quencies ν = 29,941 , 31,060 and 33,441 cm^{-1}, ch are missing in the absorption spectra of hthalene vapors [3]. It was assumed that an iden- al naphthalene preparation of guaranteed purity, used in [2] and [3], would not contain foreign urities. However, ensuing spectral investigations a number of crystals of organic compounds showed t small impurities, frequently not detected chem- lly, do show up in the absorption spectra of cry- ls and, in particular, in their luminescence. reover, the nature of the polarization bands and orption lines dependent on the impurities is ilar to the sharp polarization which is inherent the bands of the intrinsic absorption of crystals .

These facts obliged us to return anew to investi- ions of the naphthalene spectra in order to verify origin of electronic transitions in crystals. this end, we used a set of compounds of different gin and purified by different means (chemical, -crystallization from solutions, sublimation and e melting).

It appeared that the intensity of lines due to ansitions with frequencies ν = 29,941 and 31,060 cm^{-1}, in the absorption spectra of single crystals appreciable thickness (from 1 - 5 mm) grown m different preparations, differs substantially r different samples. Thus, an evolved series re- ed to the transition ν = 29,941 cm^{-1} can appear disappear in the spectra of single crystals of same thickness (about 5 mm); the line ν = 31,060 cm^{-1} can weaken and intensify. This can occur even compounds which are considered "chemically pure".

When purifying naphthalene by the zone melting thod, a slab can be obtained with layers of dif- ring purity. The transition lines ν = 31,060 cm^{-1} practically nonexistent in the spectra of single ystals (approximately 3 mm thick) picked out such a slab at a spot of maximum purity. A con- icuous polarized absorption band, corresponding to is transition, occurs in layers picked out of its ast pure portion. The luminescence of the crystals so changes simultaneously with the change in absorp- on.[1]

Such changes in the intensities of the spectral nds point to the presence of impurities in the ystals. Indeed, upon addition of β -naphthalene samples of the utmost purity at our disposal ith the least absorption in the range of transi- ons under consideration), the absorption line = 29,941 cm^{-1} is reinforced substantially, as e others associated with it also; the addition of -methyl naphthalene intensifies the line = 31,060 cm^{-1} .

In addition to these impurities, other contaminants can be present in crystals, especially those accompanying an admixture of thionaphthene to naphthalene. Bombardment of naphthalene crystals by a stream of neutrons (activation analysis [5]) led to the detection of sulfur derivatives therein.[2] It is possible that the transition ν = 33,441 cm^{-1} and all the other weakly polarized absorption lines associated with it are caused by one of these, of which the source remains obscure.

Hence, the longest wavelength electronic transitions in naphthalene crystals which are absent in the spectra of the vapors but clearly evident in the spectra of the crystals at low temperatures depend on admixtures which are difficult to detect chemically. The large scatter in the values of the quantum yields on naphthalene fluorescence in the works of different authors [6] is probably explained by the changes in intensities of the lines ν = 29,941 and 31,060, cm^{-1} for the latter of which intense luminescence of the naphthalene is started.

May 29, 1958

References

1. D. S. McClure, O. Schnepp: J. Chem. Phys., 23, 1575 (1955)
2. I. V. Obreimov, K. G. Shaballas: J. Phys., 7, 168 (1943)
3. A. F. Prikhot'ko: ZETF, 19, 383 (1948)
4. A. F. Prikhot'ko, M. T. Shpak: Opt. i Spektr., 4, 30 (1958)
5. V. I. Spitsyn, et al.: Metody raboty s primeneniem radioaktivnykh indicatorov (Methods of working with radioactive tracers) Akad. Nauk SSSR Press, Moscow, 1955
6. E. J. Bowen, E. S. Mikiewicz, F. W. Smith: Proc. Phys. Soc., A62, 26 (1949)
M. D. Galanin, Z. A. Chizhikova: ZETF, 26, 624 (1954)
M. D. Borisov, V. N. Vishnevskii: Izv. AN SSSR, Phys. ser., 20, 502 (1956)
(See translated Bulletin, Phys. Ser., published by Columbia Tech. Trans.)

1. We take advantage of the opportunity to express r gratitude to V.I. Startsev and U. V. Naboikin for pplying the naphthalene slab, produced by zone- lting, with which these experiments were conducted.

2. The experiments on the crystal bombardment and the verification of the presence of sulfur compounds in them were performed jointly with V.A. Batalin in the laboratory of M.V. Pasechnik, to whom we are grateful for this opportunity.

TOM VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar' , 1959
VOL. VI, No. 1 OPTICS AND SPECTROSCOPY January , 1959

On Intensity Distribution Along the Contour of a Self-Reversible Spectral Line

N. G. PREOBRAZHENSKII

A study of the contour of a spectral line deformed because of absorption of radiation in the light source itself, permits us to perform a quantitative calculation of the loss in the integrated light intensity and opens up the possibility of ascertaining the oscillator strengths of the lines [1,2], of assessing the temperature of a discharge [3] and the concentration and spatial distribution of emitting and absorbing atoms in the discharge space [4,5].

The theory of non-homogeneous light source, evolved by Cowan and Dieke [6], gives the essential prerequisites for the determination of the enumerated principal characteristics of spectral lines, and discharges from which these lines are radiated. These writers arrive at an intensity distribution along the line contour which has the following form in the general case:

$$J(u) = J_0 P(u)\, e^{-\mu} \Gamma(n+1) \sum_{j=0}^{\infty} \frac{\mu^{2j}}{\Gamma(n+2j+1)}. \tag{1}$$

Here $u = \nu - \nu_0$, where ν_0 is the frequency corresponding to the center of the line; the function $P(u)$ expresses the shape of the curve for an infinitely thin radiating layer; n is the degree of non-homogeneity of the source; $\mu = p\ P(u) / P(0)$ (p is an absorption parameter proportional to the concentration of the absorbing atoms averaged over the cross-section of the discharge, and to the strength of the oscillator of the line, and to the thickness of the luminous layer of the plasma); Γ is the gamma function.

The presence of the series, whose convergence slows down markedly as μ increases is a big difficulty and inconvenience in some calculations associated with the actual use of (1). We attempted to get an approximate formula for the intensity of a line capable of self-reversal, in order that this formula should, in practice, be equivalent to (1), i.e., that it give a maximum deviation from (1) known to be less than measurement errors, but that it would not contain a series and would be convenient for calculations. Hence, we concentrated first on the emission of an arc discharge for which, as pointed out in [4,5], $1 < n < 2$.

We tried to find the desired formula by first representing the series in (1) in symmetric form for the cases $n = 1$ and $n = 2$:

$$n = 1;\ \sum_{j=0}^{\infty} \frac{\mu^{2j}}{\Gamma(2j+2)} = \frac{1}{\mu} \operatorname{sh}\mu = \frac{1}{\mu}(\operatorname{ch}^2\mu - 1)^{1/2}, \tag{2a}$$

$$n = 2;\ \sum_{j=0}^{\infty} \frac{\mu^{2j}}{\Gamma(2j+3)} = \frac{1}{\mu^2}\left[\left(\sum_{j=0}^{\infty} \frac{\mu^{2j+2}}{(2j+2)!} + 1\right) - 1\right] = \frac{1}{\mu^2}(\operatorname{ch}\mu - 1). \tag{2b}$$

Consequently, by analogy with (2a) and (2b), we wrote for arbitrary n confined to the interval $1 < n < 2$:

$$J(u) = J_0 P(u)\, e^{-\mu} \Gamma(n+1) \left(\frac{\operatorname{sh}\chi}{\mu}\right)^n, \tag{3}$$

where

$$\chi = \operatorname{arch}\left(\sqrt[n]{\operatorname{ch}\mu}\right).$$

The values of the hyperbolic, exponential and gamma functions can be found from tables.

The identity of formulas (3), (2a) and (2b) for $n = 1$ and $n = 2$ is immediately obvious; the suitability of (3) for various intermediate values of the degree of non-homogeneity was carefully verified computationally in comparison with (1).

Dvornikova and Nagibina [5] demonstrated that (1) is approximated more and more exactly as μ increases, i.e., as the central portion of the line contour is approached, by the expression:

$$J(u) = J_0 P(u)\, \mu^{-n} \frac{\Gamma(n+1)}{2}. \tag{4}$$

It is clear that the same approximation will be useful for (3) also as μ increases since the following approximate equalities are thus satisfied even better:

$$\operatorname{ch}\mu \simeq \operatorname{sh}\mu \simeq \frac{e^{\mu}}{2}$$

and

$$\operatorname{sh}\chi \simeq \left(\frac{e^{\mu}}{2}\right)^{1/n}.$$

In practice (4) can be used for $\mu > 6.5$ if the errors in measuring the intensity in order to synthesize the line contour further, exceed 2%. Let us note that the root-mean-square measurement error is usually always larger than 2% both for photographic and photoelectric recording of the contour and its subsequent processing.

For small μ, i.e., for the contour wings, (1) transforms into

$$J(u) = J_0 P(u)\, e^{-\mu}, \tag{5}$$

and (3) into

$$J(u) = J_0 P(u)\, e^{-\mu}\gamma, \tag{6}$$

where $\gamma = \left(\frac{1}{n}\right)^{n/2} \Gamma(n+1)$. It is not difficult to be convinced of the fact that it is precisely for small μ (on the order of 0.1) that the greatest discrepancy between (1) and (3) is observed. Nevertheless, this discrepancy is less than 2% in the interval $1 < n < 2$ even for the most unfavorable situation ($n = 1.5$), which, as has already been pointed out, completely satisfies the practical conditions of recording and constructing the line contour. The following are the values of the coefficient γ for various n :

n ...	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7
γ ...	1.000	0.994	0.988	0.984	0.982	0.981	0.982	0.98
n ...	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5
γ ...	0.988	0.994	1.000	1.007	1.018	1.029	1.042	1.05

From the data cited it is also seen to what degree the formula (3) we proposed is applicable to compute line contours for $n > 2$. The quantity $|\gamma - 1|$ here too characterizes the maximum error upon use of (3) instead of (1), where such an error appears only during the evaluation of the contour wings.

Hence, (3) can unquestionably be used to calculate J(u) in the interval $1 < n < 2.2$ and, for measurement accuracy on the order of 5-6%, even up to $n = 2.5$. It should be noted that the source which is characterized by a degree of non-homogeneity $n = 2.5$ can be analyzed, in practice, on the basis

a model with complete spatial separation of the
nitting and absorbing atoms [6].

August 10, 1958.

References

- L. M. Biberman: Opt. i Spektr., 3, 397 (1957)
- I. M. Nagibina: IAN USSR, Phys. ser., 22, 681 (1958) (See translated Bulletin of Col. Tech. Trans.)
- H. Bartels: Z. Phys., 127, 243 (1950); 128, 546 (1950)
- I. V. Dvornikova, G. P. Startsev, M. N. Golovanova: Tr. X Conf. on Spectros., L'vov Univ. Press, 1958
- I. V. Dvornikova, I. M. Nagibina: Opt. i Spektr. 4, 421 (1958)
- R. Cowan, G. H. Dieke: Rev. Mod. Phys., 20, 418 (1948)

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROCO PY

Ianvar , 1959

VII Conference on Luminescence (Crystal Phosphors)

CH. B. LUSHCHIK, A. V. MOSKVIN

The VII Conference on luminescence, convened by the P. N. Lebedev Physics Institute of the Academy of Sciences, USSR and the Scientific Commission on Luminescence and devoted to the physics, chemistry and uses of phosphors, was held in Moscow from June 26 to July 3, 1958. More than 350 delegates from 24 cities of the Soviet Union as well as scientists from Hungary, Poland, East Germany, took part in the conference. More than 100 reports were read in the 4 plenary and 14 sectional meetings.

Although the reports were conditionally separated into primarily physical and primarily chemical groups by the organization of two sections operating in parallel, the tendency to gloss over the isolation which had long existed between physical and chemical investigations on luminescence was clearly evident in the VII Conference and was negatively expressed in the results of the work in both areas.

The reports which can apparently be referred to the physics of crystal phosphors were grouped around the following fundamental problems: 1) the nature of luminescence centers, 2) energy transport processes in crystals, 3) kinetics of combination luminescence and the nature of capture centers, 4) physical processes during excitation by an electric field, an electron beam and hard radiation.

A number of reports was devoted to the important question of the nature of luminescence centers in crystal phosphors.

Substantial results were obtained in a quantum mechanical computation of luminescence centers in a KCl-Tl phosphor (N. N. Kristofel'). The results presented in the report of N. E. Lushchik showed once again that luminescence occurs in alkali-halide phosphors activated by 'mercury-like' ions during electron transitions to the activator ions interacting with the surrounding crystal lattice. The nature of the nearest vicinity of the activator ions remains an unsolved question. It was discussed in many reports and aroused lively discussions. On the basis of an analysis of extensive experimental material, F.D. Klement arrived at the conclusion that activator ions, located at the crystal lattice sites, play a fundamental part as luminescence centers in many halide phosphors. In certain cases, surface luminescence centers can also exist. The role of surface effects in luminescence phenomena was clearly demonstrated in the interesting reports of P. Shvist and N. I. Ivanova. Starting from new data on alkali-halide phosphors activated by indium, L. M. Shamovskii and A. A. Dunina expressed the hypothesis that luminescence centers are complex, located on the crystal surfaces. It was shown in the reports of Z. A. Trapeznikova, M. L. Kats, N. E. Lushchik that luminescence centers of several kinds are possible in singly activated phosphors. The conviction was expressed, at the conference, that activator ions located near different 'point' (vacancies, impurity ions) and 'line' (dislocations) crystal defects can serve as luminescence centers.
IA. Kirs reported interesting results on the influence of uniform pressure of 7000 atm on the luminescent characteristics of Zn_2SiO_4-Mn and halide phosphors.

Z. L. Morgenshtern devoted his report to the luminescence of unactivated alkali-halide crystals which had been investigated but slightly earlier. K. K. Shvarts reported on the temperature quenching of the luminescence of alkali-halide phosphors and of the mutual relation between the optical and thermal characteristics of impurity centers. On the basis of data on the durations of the excited states of impurity centers, I. K. Pliavin' arrived at a conclusion on the metastable character of the short-time luminosity of alkali-halide phosphors.

A group of reports was devoted to the investigation of capture centers in alkali-halide phosphors (I. A. Parfianovich, F. K. Zaitov, L. IA. Uibo, P. A. Khellenurme, A. KH. Khalilov, A. M. Polonskii, and others). Characteristic of the majority of these researches is the complex investigation of excited absorption spectra, the excitation spectra optical flares and the non-isothermal relaxation of various optical characteristics.

Reports devoted to the problem of energy migration in crystals raised lively discussion. The interaction of excitons with various crystal lattice defects was investigated in the work of CH. B. Lushchik and G. G. Liid'a. Special attention was paid to the exciton mechanism of exciting luminescence and to the excitation of the luminosity of the activator ions for "band-band" transitions.

Various possible mechanisms of electron and hole processes which lead to recombination luminescence of alkali-halide phosphors, were analyzed in the reports of M. L. Kats, I. A. Parfianovich, L. M. Shamovskii, CH. B. Lushchik, KH. F. Kiaembr and I. V. Iaek. It has been shown that the usual ionization mechanism of recombination luminescence cannot explain a number of experimental results.

Various possible interpretations of the basic relaxation laws within the span of various variations of the band model of a phosphor were discussed in a group of reports devoted to the kinetics of recombination luminescence of crystal phosphors (N. A. Tolstoi and A. A. Ryskin, M. V. Fock, F. I. Vergunas, K. K. Rebane, IU. M. Popov). N. A. Tolstoi and his colleagues presented interesting material on the flare ignition of luminescence of certain zinc sulfide phosphors. The influence of infrared radiation on recombination luminescence was discussed in the reports of P. B. Iashchin (Poland) and K. S. K. Rebane. V. L. Levshin and B. M. Orlov studied the thermo-optical mechanism of electron liberation from capture levels.

It was stressed in the reports and opening remarks to the Conference that it is impossible to be limited to an analysis of electron and even of electron-hole processes in order successfully to investigate the kinetics of recombination luminescence in many cases, and exciton, sensitization, ionic, dislocation and electron-vibration processes should be taked into account as well.

Despite the evident deep relation between investigations being carried out in crystal luminescence and in semiconductor and dielectric physics, relatively few reports were devoted to the complex study of the luminescent and electrical character-

tics of phosphors (O. V. Agashkin, I. K. Vitol, . A. Oksman, U. KH. Nymm, P. E. Ramazanov). IA. Oksman presented interesting results on the pto-dielectric effects in phosphors; I. K. Vitol ed the perspective 'method of a dynamic conden- r' to study the inertial photo-polarization of psphors and to determine the sign of the current rriers.

The specific peculiarity of the VII Confer- ce, which distinguishes it from its predecessors, uld be considered the abundance and voluminous ports on electroluminescence. Prof. Nagy (Hun- ry), V. V. Antonov-Romanov, M. V. Fock and others nsidered the mechanism and kinetics of this tech- ically important kind of luminescence in interest- g reports. Interesting observations on the an- otropy of electroluminescence were made on ZnS ngle crystals synthesized by E. I. Panasiuk . E. Oranovskii, B. T. Fediushin). An investi- tion of sulfides activated by the rare earths uld permit the determination of the inherent id- tity of luminosity centers during photo and el- troluminescence (V. E. Oranovskii, Z. A Trapez- ikova).

The reports of N. N. Orlov and I. IA. Liamichev re devoted to technical applications of electro- minescence.

A number of reports, basically of applied aracter, concerned the cathode luminescence of ystal phosphates. The luminescence of phosphors, cited by hard radiation, was investigated in veral works. The report of M. D. Galanin and V. Raevskii on the temperature quenching of the minescence of ZnS-Ag excited by α-particles as heard with great interest.

The reports, pertaining to the chemistry of ystal phosphors, can first be characterized by e variety of the ideas.

The development of new luminophores on the sis of very heterogeneous chemical compounds cupied a large proportion of the reports. The mpounds obtained, having high luminosity a var- ety of spectra and inertial characteristics, nsiderably broadened the group of photo (IU. M. onov, F. M. Pekerman), cathode (M. IU. Allsalu, J. S. Blank, N. A. Gorbacheva, B. M. Gugel', L. A. Markovskii, V. P. Nazarova) and electrolumin- phors (T. K. Voznesenskaia, O. M. Kazankin, Z. I. labukova) which are very promising for technical sages. Of great interest are the crystal chem- stry extension of a class of oxygen salts with espect to luminescence (M. A. Konstantinova- hlezinger), the observations on the behavior of uropium in silicates and phosphates (IU. S. Blank, . P. Nazarova), the establishment of a relation etween the temperature quenching and the stability f the crystal lattice in tungstates (IU. M. Leonov) nd the development of a method to estimate quan- itatively the "aging" process in cathode lumin- scence (B. M. Gugel').

However, the works on the sulfide and silicate uminophors, which are studied more and used more idely in engineering, were the center of attention nd the object of the liveliest discussion. Com- unications on the interaction of "blue" and "sam- ric" centers, which confirm the sensitization and ecombination character of the luminosity of rare- arth ions in the sulfide lattice (Z. A. Trapez- ikova), additional results on excess-stoichiometric inc as the activating source of blue luminescence of a pure sulfide (A. A. Bundel') and additional results on the elementary state of silver as a sul- fide activator (A. A. Cherepnev) caused great in- terest in the question of centers of luminescence of sulfides. Apropos synthesis techniques was given a detailed review of the exchange reaction between the solid and gas phases, the part of the latter was made more precise and, especially, that of the oxygen in the formation of centers (A. A. Bundel', A. M. Gurevich, IU. M. Leonov), a thermographic analysis was made of the wurzite-sphalerite system and the existence of a new intermediate crystalline phase between them was detected (S. A. Fridman). Of the new activators, the rare-earths were exam- ined which may yield the start of a new group of technical cathode luminophors (S. A. Fridman). Finally, a report on methods of producing sulfide single-crystals, which are particularly valuable for a more rigorous study of the properties of this class of luminophors, was of great interest (E. I. Panasiuk).

Among the research on the class of silicates, it is especially necessary to note the report on the phase analysis of willemite, which would permit con- sidering luminescent zinc-manganese silicates as a metastable phase of variable composition, non-met- allic bertollides whose formation has been specified by the specific silicate structure and by peculiar- ities of the luminophor synthesis (V. V. Osiko).

The numerous reports on sublimate-luminophors and screens can be considered a peculiarity of the Conference. A noticeable step forward is also per- ceived in this area which is of interest with res- pect to its scientific and engineering prospects. The range of activators and hosts (zinc-cadmium sul- fides, sulfide-selenides) used to produce sublimate- screens has been widened considerable. The bright- ness of screen luminescence has reached a level ad- mitting of their practical usage in photo and cathode luminescence (E. IA. Arapova, E. I. Blazhnova, N. A. Vlasenko, V. V. Golubets). Works on the indus- trial synthesis of luminophors and on purification methods were relatively few at the Conference.

Reports on the use of luminescent analysis to study phase equilibria (V. V. Osiko) and on the be- havior of a reaction in the solid phase by an exam- ple of calcium aluminates (A. K. Trofimov) and mixed tungstates (IU. M. Leonov) caused lively discussions.

The VII Conference on luminescence demonstrated the successful and rapid development of a number of directions in the investigations in the physics and chemistry of crystal phosphors in the Soviet Union. At the same time, certain inadequacies were also re- vealed. Surveys of the Conference showed that there is still a certain discontinuity between the theo- retical and applied researches. On the one hand, this would lead to a lag in the development of a number of practical applications of crystal-phosphors but, on the other hand, not all the classes of lu- minophors of practical importance (and vacuum tube luminophors, first of all) would become the objects of theoretical investigations. The absence of a close enough contact between investigations being made in the region of luminescence of crystal phos- phors and in the region of semiconductor physics, which was so apparent at the Conference, can hardly be justified. The VII Conference commissioned the Scientific Soviet on Luminescence to take measures to eliminate the existing inadequacies.

TOM VI, Vyp. 1 OPTIKA I SPEKTROSKOPIIA Ianvar', 1959
VOL. VI, No. 1 OPTICS AND SPECTROSCOPY January, 1959

Optics at the International Congress on the Physics of Solids.

(Brussels, 1958)

An International Congress on the Physics of Solids and its application to electronics and telecommunications met in Brussels from June 2 to June 7, 1958. This congress, at which were gathered almost a thousand participants and guests, was one of the most important ones among the numerous conventions and conferences called in connection with the Worlds Fair of 1958. The amount of papers presented was so impressive (approximately 265), that their reading required the organization of five parallel simultaneous sessions.

In this summary we are able to check briefly only the contents of several papers pertaining to optics.

At a session entitled "Optical Applications," two papers by Seaye (France) were read, devoted to the problem of optical detection of heated solids and the telemetry of their temperatures. The thermoscopes described in the reports utilize either the effect of stimulation by infrared rays of previously activated strontium sulfide (with a rare-earth activator), or the effect of extinguishing the phosphorescence of phosphors of the sulfide group (containing iron - nickel - cobalt) under the influence of infrared rays. In the first case the maximum sensitivity is generally reached near $\lambda = 1$ micron (as an extreme, with certain sacrifices - to $\lambda = 1.8$ micron) in which case the thermoscope makes is possible to see an object heated above 300°C; in the second case it is possible to shift the infrared sensitivity toward the long wavelength and to see the object at temperatures of from 50° to 300°C. A 20% light contrast on the phosphor screen of the thermoscope may be obtained even for a difference of 1°C in the temperature of the objects.

A paper by Blé (France) described a method of high-frequency optical teletransmission in infrared cases. Modulation is accomplished by a Kerr cell with a selenium polarizer and analyzer. Lead sulfide-metal contact serves as a receiver, giving off an extremely photovoltaic effect in the infrared range and possessing a response time of less than 10^{-7} sec.

Garlick and Faithely (Great Britain) described their efforts related to infrared luminescence of phosphors. Aside from zinc and cadmium sulfides and zinc oxides (bands of luminescence in a range of 1.4 to 2.0 microns), the luminescence of mercury sulfide and cadmium telluride were studied. The former gives off one band of luminescence at 2.3 microns (290°K), the latter gives off five bands of luminescence, lying beyond the absorption edge; the structure of the spectrum depends on the structure of the crystal and on the sign of the carrier.

Loebner (USA) made a survey of the latest achievements in the field of light intensifiers, converters and image "storers," etc., utilizing new optic-electronic circuits and combinations of electroluminescent and photoconductive materials.

The session on the subject of phosphors was opened by a report by Broser and Broser-Warminsky (West Germany) on the luminescence of phosphor sulfides close to the absorption edge. In contrast to previously expressed opinions regarding the fact that "edge" luminescence is related to direct recombination of free electrons and free holes or, according to other researchers, should be ascribed to an exciton, the authors of this report cite a series of experimental data regarding luminescence and photoconductivity, from which they conclude that the "ordinary" as well as "edge" luminescence is due to the recombination of free electrons with localized holes.

A report by Rothschild (Great Britain) included a summary of new activators and co-activators of zinc and zinc-cadmium sulfides, discovered since the last summary made by the author in 1949. The speaker described spectral properties of a number of phosphors and discussed the role of the principle of charge compensation. A report by Henderson, Renby and Holstead (Great Britain) contained a detailed picture of the properties of zinc-cadmium sulfides, activated by gold.

A report by Reifel (USA) was devoted to the effect of high pressures on the luminescent properties of NaI(Tl) single crystals. The method of research was carefully developed: quartz windows, light carriers, cooling photo-multiplier, lengthy stabilizatio of temperature and pressure (to 0.1%), the possibilit of a jump in the pressure, etc. The intensity of stationary luminescence at the application of pressure (2,000 atm.) changes by almost three times. The stud of quenching under pressure indicates that the duration of the stay of electrons in the traps is increas the same number of times. The author developed a classic theory wherein the motion of ions surrounding the trap is analyzed.

Gergeli and Hongos (Hungary) devoted their repor to the analysis of losses of energy in surface films of microcrystalline phosphor layers during cathode excitation.

Hoover (USA) proposed a method of measuring weak light currents (to 10^{-12} watts) in the range of 250 - 750 millimicrons based on the calibration of the phot multiplier with the help of a light standard (a luminophor excited by a β-rays source). In the second part of the report a method to study the characteristics of high-speed cathode luminophors was describe

A total of 13 reports were read during two sessions devoted to electroluminescence. Kalman (USA) examined the influence of strong (10^3 - 10^5 V/cm) electric fields (dc as well as 60-cycle ac) on the emission, photo-conductivity and accumulation of ligh quantity in phosphors. A change in capacity and the loss in the specimen when totally exposed brings abou photo-conductivity. The application of strong constant or variable fields on phosphors (in addition to a weak field, measured by impedance) changes the valu of the apparent capacity and the loss in both the sta tionary and the relaxation regions. In addition, the variable field appears to be an effective means for quenching the excitation of phosphors (destruction of traps). As far as electroluminescence is concerned, polarization of the specimen plays an important part in a number of cases.

In an interesting report by Hahn and Zeeman (Wes Germany), an idea was developed concerning the possibility of forming a motion about fundamental processe in electroluminescent phosphors, knowing the dependence of basic characteristics of the brightness waves (asymmetry, secondary maxima and phase shifts on the strength of the field and on the temperature and elec trode form. The reporters describe the following

iel of electroluminescent mechanism" [layers, im-verished of carriers, (boundary or barrier layers) rm at the phosphor-electrode interface.] When the eld is applied in the barrier direction, the elec-ons are stripped from the atoms of the activator, ve deep into the phosphor and can be localized in aps. When the field changes direction and appears be applied in the transmission direction, the elec-ons return and recombine with the vacant activators. is yields a surface, anode luminescence near the ectrode depending on the asymmetry of the bright-ss wave. In the case of very strong fields, the rder layer can break down the electrons will be ected from a cold cathode and this will provide asymmetric surface luminescence near the cathode. minescence develops over the whole grain surface the blocking layers of the inner micro-crystals the specimen. This is "volume" luminescence, al-ough actually only the surface is luminescent. In case of insulated electrodes, "volume" lumines-nce produces symmetric brightness waves. Secondary xima are connected with the relaxation of the polar-ing field. When the temperature is raised, this eld and the secondary maxima disappear.

Ivey (USA) devoted his report to the question the influence of an electric field on phosphors cited by light or X-rays. As is known, an electric eld may cause quenching as well as enhancement of e luminescence of phosphors (not connected with dition of electroluminescence). Quenching is ex-ained either by non-radiating transitions, caused the field, or by filling also under the influence the field, of the ionized centers of luminescence. e enhancement of the luminescence is apparently con-cted with the fact that the field eliminates elec-ons from those traps from which the non-radiating ansitions generally emanate; it is also possible at the enhancement is connected with a change in nsity of the electrons (if in this case the non-nearity of the kinetics is allowed). Thornton SA) concentrated in more detail on the effect of hancement, assuming, just as the preceding author, at the quenching during the combined action is nnected with the lowered value of the radiating combination and is not related to the mechanism the electroluminescence.

The founder of electroluminescence, George estrian (France) offered a paper (accompanied by ffective experiments) on the phenomena of "memory" certain sulfides (type ZnS — CdS · Mn, X) when eir X-ray-luminescent response is enhanced with e help of an electric field. Enhancement of elec-roluminescence by an electric field may be noted ven in the case of extremely weak alternating fields ≈ 50 v/cm). When the fields are strong, the en-ancement is masked by ordinary electric quenching. e "memory" effect was most interesting. By a oint effect of X-rays (even very weak ones) and an lectric field, it was possible to "sensitize" phos-nors, which, even after remaining in the dark for a engthy period of time, will glow brighter than non-sensitized" phosphors after excitation by X-rays or several seconds.

In a report by Pengeau (France), the same effect f enhancement of X-ray luminescence by a field was tudied from a kinetic aspect.

V. V. Antonov-Romanovskii (USSR) reported a eries of experiments in connection with electro-uminescence of zinc sulfide powders and single rystals. In these experiments, directed towards explanation of the basic mechanism of electroluminescence, kinetic processes are successfully utilized, as is the comparison of the regularity of luminescence for various kinds of excitation.

Reports by Fritsche (East Germany), Larach and Shrader (USA) and Thornton (USA) were devoted to certain chemical aspects of electroluminescence.

Among reports, read during the sessions, devoted to the "theory of solids" and to "miscellaneous problems," reports by Classens (Holland) and S. Nikitine (France) should be noted. Classens showed that a model of a photo-semiconductor with two types of surfaces in the forbidden zone can explain super-linear luminescence and photo-conductivity, activation and quenching. This cannot be applied to detailed distribution of local surfaces in the forbidden zone, as it is done in Rose's theory.

In Nikitine's report there were summed up results of studies of "exciton" spectra of absorption of a number of crystals. The spectra may be separated into three different classes. Two of them may be very well described by the exciton spectra theory, predicting exactly two spectra - one permissible, the other barely permissible. The spectra of the third class have so far not been defined in theory.

The exciton problem did not occupy the center of attention of the participants of the congress: among "exciton" papers only a report by Balkansky (France), dealing with the diffusion of excitons in a semiconductor, may be mentioned.

On the whole, the congress was highly successful, due, in no small measure, to the energetic and self-less efforts of its practical organizers.

The delegation of Soviet scientists, active in the work of the congress, consisted of V. V. Antonov-Romanovskii, B. M. Vul, D. N. Nasledov, A. N. Terenin and N. A. Tolstoi.

(signed) N. A. Tolstoi.

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar' , 1959
January , 1959

Anniversaries and Dates

M. A. EL'IASHEVICH

On his 50th Birthday

August 21, 1958, marked the 50th birthday of Mikhail Alexandrovich El'iashevich, the prominent representative of the Spectroscopic school, twice-laureate of the Stalin Prize, and active member of the Academy of Science of the Belo-Russian SSR.

M. A. El'iashevich achieved great creative success in his thirty years of scientific and pedagogic activity.

After graduating from secondary school in 1925, Mikhail Alexandrovich entered the Department of Physics of the State University of Leningrad. From 1928 on, while still a student, M. A. El'iashevich started working on scientific subjects under the immediate supervision of A. N. Terenin. The first efforts of Mikhail Alexandrovich were experimental in nature.

After graduating from the University in 1930, Mikhail Alexandrovich entered the Institute for Chemical Physics. In 1935 he transferred to the State Optical Institute, joining the Group for Theoretical Spectroscopy, and in 1937 successfully presented his graduating thesis on the subject "The Rotational-Vibrational Energy of Polyatomic Molecules."

Constantly enlarging his field of scientific studies and promptly answering the call of the rising requirements of science and technology, Mikhail Alexandrovich began to study the spectroscopy of rare-earth elements. Following the initiative of D. S. Rozhdenstvenskii, he carried out a thorough, critical analysis of all literary data concerning this most important group of chemical elements. As a result of this great and fecundary work, there appeared in 1940 a monograph by M. A. El'iashevich, entitled "Spectra of Rare Earth Atoms." In this work by Mikhail Alexandrovich, his aptitude in generalizing experimental data is displayed. Several sections of the monograph are original and established fundamental principles for the interpretation of complex spectra.

From 1939 on, Mikhail Alexandrovich's work is connected with the application of spectroscopy to analysis of the structure of molecules. He was able to develop simple and universal methods of computation of vibrational spectra of polyatomic molecules. The fecundary work of this period was concluded with the presentation in 1944, of his doctor's thesis and the writing of a two-volume monograph (jointly with M. A. Vol'kenshtein and B. I. Stepanov) entitled "The Vibrating Molecule," which was honored by a Stalin Prize in 1950. The results of this work received most extensive circulation. In 1949, after successfully completing important scientific studies, Mikhail Alexandrovich received the Order of Lenin and for the second time attained the status of Laureate of the Stalin Prize.

From 1948 to 1955, M. A. El'iashevich worked in the Leningrad Institute for Precision Mechanics and Optics and also in the Pedagogic Institute named after Hertz. Here he continued to develop the theory of spectra of complex atoms, concluding it in 1953 with a new monograph, entitled "Spectra of Rare Earths", differing considerably in volume and contents from the first monograph devoted to rare earths. This monograph encompasses spectra of lanthanides as well as actinides.

From 1955 to 1956, M. A. El'iashevich was in charge of the Optics Laboratory of the Institute of Chemical Physics of the Academy of Science of the USSR where he was occupied with the study of high-temperature optics and spectroscopy.

In March of 1956, Mikhail Alexandrovich was elected Academician of the Academy of Science of the USSR. In Minsk he worked successfully in the field of radio-spectroscopy and concurrently completed one more monograph, "Atomic and Molecular Spectroscopy." It includes a generalization of the copious experiments of Mikhail Alexandrovich and those of many spectroscopic associations.

In addition to his tireless scientific activity, Mikhail Alexandrovich also carried on important pedagogical work. Students know him as an outstanding pedagogue, skillfully instructing them in contemporary physics, innoculating them with the habit of scientific work. The number of courses taught by Mikhail Alexandrovich is very large, which beautifully characterizes his profound erudition and versatility.

Since 1931, Mikhail Alexandrovich has taken an active part in the publishing field, serving as science editor of a variety of original and translated monographs. From 1946 to 1948 he was chief editor of the Leningrad branch of Gostekhizdat (Government Technical Publishing Office). At present he is a member of the editorial staff of Fizmatgiz (Government Publishing Office for Physics and Mathematics), acting chief editor for the "Engineering and Physical Journal" and member of the editorial staff of the Optics and Spectroscopy Journal."

The editorial staff of the "Optics and Spectroscopy Journal," on behalf of all Soviet spectroscopists, heartily congratulates Mikhail Alexandrovich and wishes him many years of further successful work.

ABBREVIATIONS OFTEN ENCOUNTERED AND USED HEREIN

Journals and Institutions

DAN USSR	Doklady Akademii Nauk USSR (Reports of the Academy of Sciences of the USSR)
DAN UkrSSR	Dopovidi Akademii Nauk UkrSSR (Reports of the Academy of Sciences of the Ukraine SSR)
DAN ArmSSR	Doklady Akademii Nauk ArmSSS (Reports of the Academy of Sciences of the Armenia SSR)
IAN USSR	Izvestiia Akademii Nauk USSR (Bulletin of the Academy of Sciences of the USSR)
	Seriia fizika (Physics series)
	Seriia matematika (Mathematics series)
	Otdelenie khimicheskikh nauk (Section of chemical sciences)
OiS	Optika i Spektroskopiia (Optics and Spectroscopy)
PiTE	Pribory i Tekhnika Eksperimenta (Instruments and Techniques of Experiment)
AE	Atomnaia Energiia (Atomic Energy)
AZ	Astronomicheskii Zhurnal (Astronomy Journal)
FMM	Fizika Metallov i Metallovedenie (Physics of Metals and Metallography)
Radiotekh.	Radiotekhnika (Radio Engineering)
RiE	Radiotekhnika i Elektronika (Radio Engineering and Electronics)
UK	Uspekhi Khimii (Progress in Chemistry)
UFN	Uspekhi Fizicheskikh Nauk (Progress in Physical Sciences)
UFZ	Ukrainskii Fizichni Zhurnal (Ukraine Physical Journal)
ZETF	Zhurnal Eksperimental'noi Teoreticheskoi Fiziki (Journal of Experimental Theoretical Physics - JETP)
ZTF	Zhurnal Tekhnicheskoi Fiziki (Journal of Technical Physics)
FTT	Fizika Tverdogo Tel (Solid State Physics)
ZFKh	Zhurnal Fizicheskoi Khimii (Journal of Physical Chemistry)
ZOKh	Zhurnal Organicheskoi Khimii (Journal of Organic Chemistry)
ZNKh	Zhurnal Neorganicheskoi Khimii (Journal of Inorganic Chemistry)
Tr.	Trudy (Transactions, as for instance, Tr. FIAN)
FIAN	Fizicheskii Institut Akademii Nauk (S. N. Lebedev Physical Institute of the Academy of Sciences USSR)
Sb.	Sbornik (Collection, as for instance, Fizich. sb. L'vovskogo universitet)
Fizich. sb.	Fizicheskaia sbornik (Physics Collection)
Uch. Zap.	Uchenye Zapiskii (Scientific Records)
Vestn.	Vestnik (Herald or Messenger)
FTIAN	Fiziko-Tekhnicheskii Institut Akademii Nauk (Physical-Technical Institute of the Academy of Sciences)
GITTL	Gostekhizdat - Gosudarstvennoe Izdatel'stvo Tekhniko-Teoreticheskoi Literatury (State Publishers of Technical-Theoretical Literature)
GIFML	Fizmatgizdat - Gosudarstvennoe Izdatel'stvo Fiziko-Matematicheskoi Literatury (State Publishers of Physical-Mathematical Literature), formerly Gostekhizdat
IL or IIL	Izdatel'stvo Inostrannoi Literatury (Publishers of Foreign Literature)
Izd. AN USSR	Izdatel'stvo Akademiia Nauk USSR (Academy of Sciences Press)
ZL	Zavodskaia Laboratoriia (Factory Laboratory)
GOST	Gosudarstvennyi Obshchesoiuznyi Standart (All-Union State Standard)

Apparatus

IKS-11	Infrakrasnyi spektrofotometer (Infrared spectro-photometer)
VIKSM-3	Vakuumnoe Infrakrasnyi spektrometer (Vacuum Infrared Spectrometer)
SF-4	Spektrofotometer (spectro-photometer)
DFS-2	Difraktsionnyi Spektrograf (Grating Spectrograph)
DG-1	Generator dygi peremennogo toka (AC Arc Generator)
FEU	Fotoelektronnyi Umozhnitel' (Photo-electron Multiplier)

INFORMATION FOR AUTHORS (Russian)

The following rules apply to manuscripts being submitted to the Editors.

1. Papers which are the results of research conducted in institutions must certainly have the direction of the appropriate institution.

2. The paper should be explained as briefly as possible, compatible with clarity of explanation, and in final form. Repetition of tabular or graphical data in the text should be avoided, as should the representation of numerical results in the form of tables and graphs simultaneoulsy. Each paper should not exceed 12 pages of typewritten text, including figures. Two copies of both text and graphical material should certainly be provided.

3. The paper should start with a brief annotation mentioning the purpose and results of the research. The annotation and the section CONCLUSIONS (if such there be in the paper) must not, however, duplicate each other.

4. The paper should be typewritten on one side of the page, handwritten inserts are not permitted. Formulas should be written legibly in ink. All the manuscript pages should be numbered. The tables and references should be written on separate sheets.

The papers must certainly be signed by the author and when there are several authors, by all of them.

5. In order to avoid confusion and errors, explicit distinction should be made between capital and small letters in the formulas. When the upper and lower case letters are identical in outline but differ only by their size (C and c, I and i, K and k, O and o, P and p, S and s, U and u, V and v, W and w), the upper case letters should be double-underlined (for example, -S) and the lower case letters should receive a double-overline (for example, $\bar{\bar{s}}$). It is necessary to differentiate between the letter O (capital), o (small) and) (zero), where the letters O and o are differentiated by the double underlining and overlining while the zero remains unmarked. The letters I and J should also be differentiated; in order to write the letter I in the manuscript as the Roman one underlined doubly. Greek letters are emphasized by red crayon, vectors by blue or black pencil.

6. Footnotes should be enumerated in order over the whole paper. The references are placed in one list at the end od the paper with the text mention indicated by ordered numbers enclosed in square brackets (for example [1]). The list of references should be composed as follows: a) For journal articles, the initials and surname of the author (or authors), the journal designation (only usually accepted abbreviations to be used), the volume number (underlined by a wavy line), the starting page and the year should be indicated; b) for books it is necessary to indicate the initials and surname of the author (authors), the complete title of the book, the place and year of publication (for foreign books, indicate the data on the Russian translation if such there be).

7. The editors request the authors to use the least number of figures possible.

Figures and photographs should be presented separately from the manuscript and must in no case be glued to the original. It is desirable to provide the figures with clarifying captions which should be collected on a separate sheet. On the back of each figure (and photograph) there should be mentioned: Surname of the author (authors), title of the paper, figure number. Inscriptions on the figures should, if possible, be replaced by numbers (or letter notations) explained in the caption to the figure (or in the text).

8. The editors request the authors to indicate the places in the manuscript which can be in smaller type.

9. There should be indicated at the end of the paper: The exact address, surname, given name and patronymic of the author as well as the home or office telephone number.

10. In case the paper is returned to the author for revision, the date of receipt should be considered the date the Editors receive the final text.

11. The Editors will provide the author with 50 unbound reprints, free.

The journal is published monthly in two volumes per year (6 issues per volume).

This being the first issue of the translated rsion of the Russian journal Optika i Spektro-opiia, the Optical Society of America has kindly nsented to permit us to explain our part in the ecution of this project and to list our aims.

We were approached by the Translations mmittee of the Society in April, 1959 with the quiry as to whether we could undertake the anslation of this journal with the idea of king it a current, or simultaneous, translation July, 1959. We, of course, replied that al-ough it was impossible because too many factors yond our control were involved, we would certainly willing to try.

The Society then presented us with two copies issue number 1 for 1959 of the Russian journal d told us to go ahead. This publication is the uit of that meeting.

Since it was agreed that speed was of great portance, we have proceeded, sometimes under our n initiative, to produce as fine a product as we uld in as short a time as possible. There will doubtedly be many defects in this first issue t it is our hope that these will be brought to r attention so that they can be eliminated from ture issues.

As to the status of future issues, we have quired a copy of all the original Russian and are proceeding as fast as possible. We have gaged translators and editors from among the mbers of the Society and their whole-hearted operation is helping to make the task easier. wever, there is still need for additional, mpetent help so that we could actually do what have set out to do, namely, publish a simultaneous anslated version.

We should like to compliment the Society, too, its progressive and far-sighted policy in making is translation available to each member and sub-riber and thus permitting more of the scientific mmunity to keep current with research in their ecialties.

At this time, we should like to present our eas on what is the job we have to do. In past ars we have carefully perused the various trans-ted journals and have estimated their good and ad qualities from the viewpoint of scientist and ibrarian users. Hence, we have arrived at rather efinite ideas about what should be included in a anslated journal in order that it might be made more valuable research tool and source of inform-ion. We shall first list our ideas and then the easoning behind them.

In our opinion, in addition to being current, translated journal should have the following eatures (from front to back):

1. A title page designating the transliterated nd translated name of the journal; the volume and ssue numbers and date of publication of the original ournal; the volume number and date of the trans-ation (if all volumes of the journal from the irst are not being translated); the editorial oards, both Russian and American, responsible for he material appearing in the magazine.

2. A transliterated and translated table of ontents including the pagination of both the ussian original and of the translation.

3. Literate, carefully edited (prior to publication) translations of the journal articles with particular care being taken that the ideas and, perhaps, the style of the author are retained. Where the editors or translators have specific comments to make, they should be included as footnotes to the translation and credited to the commentator.

4. References carefully checked by an experienced librarian from all available sources. References to be listed in the nomenclature of the original language. In the case of Russian books, both the transliterated and translated titles should be provided. If the reference is a Russian translation of a Western book, the original should be referenced with an indication that the translation was used.

5. Indications of the existence of translations of foreign references and where and if available.

6. A listing of abbreviations of journals, institutes and apparatus and their full meaning.

7. If possible, the addresses of the authors.

The reasoning behind the above seven points is the following.

1°. When volumes are bound and covers removed, all pertinent information will be contained on the inserted title page.

2°. Such a table of contents will enable skeptics and purists to refer back to the original to check on the accuracy of the translation. It would also enable librarians provided with a Russian title to find the translated reference.

We shall use the Library of Congress transliteration scheme throughout, since we feel some sort of standardization is necessary. This may offend some scientists whose names have been traditionally transliterated otherwise, but we feel that the Library of Congress was the first to catalog available Russian scientific translations and their scheme has been accepted.

3°. Such translations will undoubtedly appear foreign and not attuned to American ears to many readers but we should like to point out that the research is not American nor described by Americans. Besides, in some cases it was not even written by Russians. To the Ukrainians, Belorussians, Latvians, Uzbeks, Esthonians, etc., Russian is a second language and not always an easy one in which to communicate. We also feel the author should be allowed to speak for himself and not through the mouth of an interpreter.

4°. All references should be checked because Russian typesetters and proof-readers seem to be particularly lax about allowing errors, especially with respect to foreign references, to appear in print. It is also possible that the author did not have direct access to the reference listed but had to make use of other sources such as abstracting journals, etc. In other words, the references may be second-hand and may have become garbled in the transmission.

5°. An indication of whether a translation exists or not is helpful to those who would like to go back to the original sources on which the research may be based. In particular, since this is a Russian journal, there will undoubtedly be

many references to Russian rather than to Western research.

6°. This material, namely, the abbreviations and their full meanings is mainly of interest for information purposes and to enable us to cite references in more compact form.

7°. The addresses of authors is also of interest for just informational purposes. However, since the author s affiliation is not given in this journal, we shall have a difficult job in locating them. We shall do whatever we can about this and would welcome assistance from any source.

Now, what have we been able to accomplish in the way of satisfying these seven requirements in this first issue. We know that we have fallen below our aims in several places. However, let us review these points one by one and see what our score would be.

1. We have a title page. However, librarians will be unhappy because we have not been able to figure out how to indicate that this volume is the first to be translated without confusing the numbering system. Of course, the perfect solution would be to have all previous five volumes translated as well.

2. We have the transliterated and translated table of contents with both paginations.

3. In our opinion, our translations are literate and we are certain that they have been carefully edited by competent people.

4. A trained librarian, Miss Eileen Kibrick, has done an excellent job of checking the references. If there are still errors in the listings, it is certainly not the fault of Miss Kibrick but should be attributed to the short span of time we allotted ourselves for the publication of this first issue.

Also because of the time deadline, we have not succeeded in listing the foreign references as we think they should be.

5. We have made use of whatever information we have in order to list existing translations. In some cases, particularly in the case of the translation of the Izvestiia (Bulletin), we have listed material as having been translated, whereas the translation may not be published until later in the year. Our reasoning here is that this translation will have continuing use and should be used after the particular issue of the Izvestiia has been translated.

In subsequent issues we shall make use of an extensive card file of translations and we shall make every effort to list every translation we can. However, we know that there must be translations in existence which are not in our card files. We should appreciate receiving listings of any such so that we could increase this service.

6. There is a partial listing of abbreviations of journals and institutes. The journal listing will probably remain the same but we hope to add abbreviations of new institutes and apparatus each month. In the main, we have found that their apparatus is usually designated by the initials of the Russian words describing the apparatus.

7. In this issue, we have not listed any addresses although we think we know the affiliation of several of the authors. We shall, instead, include these addresses in the next issue.

It is our earnest hope that we have done a job which reflects credit on the Society and ourselves as well. We do not mean to imply that we alone are capable of executing the project nor that we have devised the perfect format for a translated journal. We do feel that we have tried to think of all the requirements that a translation should have and that we have met them successfully. If not, we should certainly like to hear about it. We should also like to be able to turn out a magazine which will be used, with profit, by as many as possible.

MORRIS D. FRIEDMAN, INC.
POST OFFICE BOX 35
WEST NEWTON 65, MASS.

Corinne Friedman

Corinne Friedman, Pres.

Morris D. Friedman

Morris D. Friedman, Tech. Dir.

G. KAMINSKII
K voprosu o "ballisticheskov" metode issledovaniia zatukhaniia fosforestsentsii 103
On the question of the ballistic method to investigate the decay of phosphorescence 62

PASTRNIAK
Spektr infrakrasnogo pogloshcheniia zakisi medi 107
Infrared absorption spectrum of cuprous oxide 64

G. GONIKBERG, KH. E. STERIN, S. A. UKHOLIN, A. A. OPEKUNOV, V. T. ALEKSANIAN
Poluchenie spektrov kombinatsionnogo rasseianiia pri vysokikh davleniiakh 109
Production of Raman spectra at high pressures 66

A. LOGINOV
Poluchenie spektra pogloshcheniia AlO metodom elektricheskogo vzryva provolochki v vozdukhe pri atmosfernom davlenii 111
Production of the absorption spectrum of AlO by the method of electrically exploding a wire in air at atmospheric pressure 67

. I. RYSKIN
Ob infrakrasnykh spektrakh pogloshcheniia nitratov v nevodnykh rastvorakh 113
On the infrared absorption spectra of nitrates in anhydrous solutions 69

. F. GROSS, L. G. SUSLINA
Monokristally ZnS i spektr ikh kraia pogloshcheniia pri nizkikh temperaturakh 115
Monocrystals of ZnS and the spectrum of their absorption region at low temperatures 70

. P. BELIKOVA
Dlitel'naia liuminestsentsiia kristallov dibenzila i difenilamina pri foto- i β -vozbuzhdenii 117
Prolonged luminescence of dibenzyl and diphenylamine crystals under photo- and β-excitation 72

. F. PRIKHOT'KO, M. T. SHPAK
O prokhozhdenii nekotorykh elektronnykh perekhodov v kristallakh naftalina 119
On the origin of certain electronic transitions in naphthalene crystals 73

. G. PREOBRAZHENSKII
O raspredelenii intensivnosti po konturu spektral'noi linii, sposobnoi k samoobrashcheniiu 120
On intensity distribution along the contour of a self-reversible spectral line 74

KHRONIKA
NEWS

H. B. LUSHCHIK, A. V. MOSKVIN
VII Sovexhchenie po liuminestsentsii (Kristallofosfory) 122
VII Conference on luminescence (Crystal Phosphors) 76

. A. TOLSTOI
Optika na mezhdunarodnom kongressa po fizike tverdogo tela (Briussel', 1958 g) 124
Optics at the international congress on the physics of solids (Brussels, 1958) 78

IUBILEI I DATY
ANNIVERSARIES AND DATES

.. A. EL'IASHEVICH (K piatidesiatiletiiu so dniia rozhdeniia) 127
M. A. EL'IASHEVICH (On his fiftieth birthday) 80

Abbreviations of Russian journals and institutes 81
Information for authors (Russian) 82
Letter from the publisher 83

Printed by Blackburn Printing Company, Concord, Mass.

TOM VI, Vyp. 1
VOL. VI, No. 1

OPTIKA I SPEKTROSKOPIIA
OPTICS AND SPECTROSCOPY

Ianvar', 1959
January, 1959

SODERZHANIE

IU. P. DONTSOV
Izotopicheskoe smeschchenie v spektre ZrI 3

G. V. VEINBERG
Izotopicheskii analiz po spektru pogloshcheniia iodistoi medi 9

M. P. VANIUKOV, A. A. MAK, V. R. MURATOV
Vremennye spektry izlucheniia iskrovogo razriada v inertnykh gazakh 17

T. K. REBANE
Ob elektronnykh spektrakh pogloshcheniia alifaticheskikh polisul'fidov 24

M. S. BRODIN, A. F. PRIKHOT'KO, M. S. SOSKIN
O nesobliudenii dispersionnykh sootnoshenii Kramersa-Kroniga v sluchaw molekuliarnykh kristallov pri razlichnykh temperaturakh 28

A. I. FINKEL'SHTEIN
Opticheskoe issledovanie molekuliarnogo stroeniia proizvodnykh s-triazina. IV. Spektry pogloshcheniia v infrakrasnoi oblasti soedinenii s kondensirovannymi iadrami s-triazina-proizvodnykh tsiamellurovoi kisloty 33

V. A. KOLESOVA
Infrakrasnye spektry pogloshcheniia silikatov soderzhashchikh Al , i nekotorykh kristallicheskikh aliuminatov 38

N. A. CHUMAEVSKII, V. M. TATEVSKII, IU. K. IUR'EV
Spektry pogloshcheniia i spektry kombinatsionnogo rasseianiia selenofena i ego metilgomologov 45

A. I. SOKOLOVSKAIA, S. G. RAUTIAN
Vliianie pokazatelia prelomleniia rasseiavaiushchei sredy na intensivnost' linii kombinatsionnogo rasseianiia sveta 51

V. L. LEVSHIN, E. G. BARANOVA
Issledovanie prirody kontsentratsionnogo tusheniia liuminestsentsii krasitelei v raznykh rastvoriteliakh i razdelenie razlichnykh vidov tusheniia 55

S. F. KILIN, I. M. ROZMAN
O zakone vysvechivaniia polistirola pri vozbuzhdenii elektronami 65

S. F. KILIN, I. M. ROZMAN
Vliianie reabsorbtsii na dlitel'nost' fluorestsentsii organicheskikh veshchestv 70

I. N. SHKLIAREVSKII, V. G. PADALKA
Izmerenie opticheskikh postoiannykh medi, zolota i nikelia v infrakrasnoi oblasti spektra 78

F. I. FEDOROV
K teorii opticheskoi aktivnosti kristallov. I. Zakon sokhraneniia energii i tenzory opticheskoi aktivnosti 85

KRATKIE SOOBSHCHENIIA

K. N. TARASOV
Interferentsionnye zerkala na aliuminievoi podlozhke 94

E. M. AKIMOV, I. P. MALKOV
Opredelenie temperatury vakuumnoi iskry 96

A. N. FAIDYSH, V. L. ZIMA
Vliianie kontsentratsii primesi na zavisimost' kvantovykh vykhodov liuminestsentsii ot tolshchiny kristallov antratsena 98

V. M. PIVOVAROV
Vliianie vnutrennogo polia na intensivnost' kombinatsionnogo rasseianiia 101

CONTENTS

Isotopic shift in the spectrum of ZrI 1

Isotopic analysis of the absorption spectrum of copper iodide 4

Time resolved spectra of the radiation from a spark discharge in inert gases 8

On the electronic absorption spectra of the aliphatic polysulfides 11

On the breakdown of the Kramers-Kronig dispersion relations in molecular crystals at various temperatures 14

Optical investigation of the molecular structure of s-triazine derivatives. IV. Infrared absorption spectra of compounds with condensed nuclei of s-triazine derivatives of cyameluric acid 17

Infrared absorption spectra of the silicates containing aluminum and of certain cryatalline aluminates 20

Absorption spectra and Raman spectra of selenophene and its methyl homologues 25

Influence of the refractive index of a dispersing medium on the Raman spectrum line intensity 29

A study of the concentration extinction of dyes in various solutions and isolation of various types of extinction 31

On the fluorescence law in polystyrene on excitation by electrons 37

Effect of reabsorption on the fluorescence lifetimes of organic substances 40

Measurements of the optical constants of copper, gold and nickel in the infrared region of the spectrum 45

On the theory of optical activity in crystals. I. The law of conservation of energy and the optical activity tensors 49

BRIEF REPORTS

Interference mirror on an aluminum substrate 54

Determination of the temperature of a vacuum spark 56

Influence of impurity concentration on the quantum efficiency of luminescence as a function of anthracene crystal thickness 58

Influence of the internal field on Raman spectrum intensity 60